THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 13, NUMBER 11 NOVEMBER, 1945

Thermodynamics of Dilute Solutions of High Polymers[1]

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(Received June 25, 1945)

Whereas extensive efforts have been directed recently toward improving the mathematical exactness of the statistical mechanical theory of polymer solutions, fundamental limitations set by the nature of the physical approximations have not received adequate attention. A careful comparison between theory and experiment in dilute solutions reveals a large discrepancy between the calculated and the observed departures from the ideal entropy of dilution. The assumption of random occupancy of lattice sites by polymer segments, which is employed in previous treatments, is at fault. In very dilute solutions of high polymers the solution is microscopically discontinuous. Two regions of the volume can be distinguished: one is totally unoccupied by segments of polymer molecules; the other consists of regions encompassed by the irregularly coiled polymer molecules. In the latter the concentration of lattice cells occupied by polymer segments is determined by the configuration of the polymer molecule, being independent of the over-all average concentration.

The above concepts have been employed in the formulation of a new statistical mechanical theory of the thermodynamic properties of very dilute high polymer solutions. The deviation from ideality, e.g., the slope of the osmotic pressure: concentration ratio plotted against concentration, is related to the "effective volume ratio" of the irregularly coiled solute molecule. This ratio, or "swelling factor," can be estimated from the intrinsic viscosity of the polymer. Satisfactory agreement between theory and experiment is obtained in this way. The comparatively small deviations from ideality which are observed for protein molecules, not extremely dissymmetric in shape, receive semi-quantitative interpretation under the present theory. The failure, of the van Laar expression to account for heats of mixing in polymer solutions at all concentrations is a necessary consequence of the discontinuities in the dilute region.

INTRODUCTION

THE striking "abnormalities" in the equilibrium properties of high polymer solutions are known to arise from "non-ideal" entropies, which in turn are a consequence of the extreme dissimilarity in the sizes of the molecules of solvent and solute.[2,3] Recent statistical mechanical treatments of these mixtures[4–8] have met with a noteworthy degree of success in accounting for their osmotic behavior, vapor pressures, and solubility relationships. Nevertheless, definite limitations on these theories become apparent on close examination of their foundations and of their correlation with the available experimental data. The present paper is concerned with these limitations. In particular, it is concerned with the shortcomings of the existing statistical mechanical treatments in the region of low concentrations of polymer, where discrepancies between theory and experiment are greatest.

[1] Presented before the Division of Physical and Inorganic Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pennsylvania, September 1943.
[2] K. H. Meyer, Zeits. f. physik. Chemie **B44**, 383 (1939); K. H. Meyer and A. J. A. van der Wyk, Helv. Chim. Acta 23, 488 (1940); K. H. Meyer, *Natural and Synthetic Polymers* (Interscience Publishers, Inc., New York, 1942), p. 582.
[3] E. Hückel, Zeits. f. Elektrochemie **42**, 753 (1936).
[4] M. L. Huggins, J. Chem. Phys. **9**, 440 (1941); J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **43**, 1 (1942).
[5] P. J. Flory, J. Chem. Phys. **9**, 666 (1941); **10**, 51 (1942).
[6] A. R. Miller, Proc. Camb. Phil. Soc. **39**, 54, 131 (1943).
[7] W. J. C. Orr, Trans. Faraday Soc. **40**, 320 (1944).
[8] E. A. Guggenheim, Proc. Roy. Soc. **183**, 203, 213 (1944).

COMPARISON OF THEORETICALLY DERIVED PARTIAL MOLAL ENTROPIES

The various current theoretical treatments of polymer solutions[4-7] are based on the same idealized model, which consists of a pseudo-lattice each cell of which may be occupied either by a molecule of solvent or by an element of the chain molecule (solute) equal in size to the solvent molecule. This element will be referred to here as a segment. The chain molecule consists of a sequence of x segments, which necessarily must occupy a sequence of x consecutively adjacent cells of the lattice. It is ordinarily assumed that the segments are flexibly connected so that the $(i+1)$th segment of the chain is free to occupy any of the z cells (where z is the coordination number of the lattice) surrounding the cell occupied by the ith segment of the chain, the one occupied by the $(i-1)$th segment excepted of course. This assumption is unimportant in determining the thermodynamic properties of *solutions*, so long as the degree of flexibility is independent of concentration;[4] the same equations are derived even for stiff rods totally devoid of flexibility.[6]

For the statistical treatment of the problem it is convenient to consider that the polymer molecules are successively added to the empty lattice; solvent molecules may then occupy the remaining vacant cells. The expected number of configurations available to the jth polymer molecule to be added is obtained by taking the product of the following factors: the number of locations available to the first segment of the chain, which number will be equal to the number of vacant cells in the lattice; the expected number of vacancies among the z cells[9] surrounding a given vacant cell, which gives the expected number of cells available to the second segment; the expected number of vacant cells available to the third segment, the second having been assigned a definite location in the lattice; etc. The writer[5] introduced the simplifying approximation that the average occupancy of the cells surrounding the cell assigned to the ith segment (and therefore known to have been a vacant cell) will be the same as the over-all concentration of polymer segments in the entire lattice. In other words, the fact that the cell to which the ith segment is to be assigned is known to be vacant was assumed as an approximation to have no effect on the expected number of vacancies in the immediately surrounding cells. The total number of configurations of the system as a whole was obtained as the product of these expected numbers of configurations available to each successively added polymer molecule.

In this way the following equation was derived for the entropy of mixing N moles of randomly disoriented polymer molecules with n moles of solvent[5]

$$\Delta S = -R[n \ln v_1 + N \ln v_2], \tag{1}$$

where v_1 and v_2 are volume fractions of solvent and solute, respectively, i.e.,

$$v_1 = 1 - v_2 = n/(n+xN). \tag{2}$$

In accordance with previous definition x is equal to the ratio of the molar volumes of solute and solvent. The partial molal entropy of the solvent $\Delta\bar{S}_1$ is obtained by differentiating Eq. (1) with respect to n, keeping in mind that v_1 and v_2 are functions of n as given by Eq. (2).

$$\Delta\bar{S}_1 = -R[\ln (1-v_2) + (1-1/x)v_2], \tag{3}$$

or

$$\Delta\bar{S}_1 = Rv_2(1/x + v_2/2 + v_2^2/3 + \cdots). \tag{3'}$$

Huggins[4] in his treatment of the problem took into account two factors admittedly neglected by the writer:[5] (a) the exclusion of those impossible configurations in which two segments of the same chain would occupy the same cell of the lattice; and (b) the departure of the frequency of occurrence of polymer segments in cells surrounding a given cell known to be vacant (i.e., unoccupied by a polymer segment) from the over-all average concentration of polymer segments. Thus, if a given cell is known to be vacant, there is a better than average chance that a specified adjacent cell is vacant also; conversely, if a cell is known to be occupied by a polymer segment, then a neighboring cell has an enhanced probability of being likewise occupied by a polymer segment, which may belong to the same or to a different polymer molecule. With these two factors taken into account, Huggins obtained for the partial

[9] In the present paper the more widely accepted symbol "z" has been used for the coordination number of the lattice, in place of the "γ" previously used by the writer.

molal entropy of the solvent

$$\Delta\bar{S}_1 = -R[\ln(1-v_2) - (1-1/x)(z'/2)\ln(1-2v_2/z')], \quad (4)$$

where z' is a corrected "coordination number" given when x is large by

$$z' = (z-2f_0)/(1-f_0), \quad (5)$$

where f_0 is the probability that a given cell adjacent to the cell occupied by the ith segment (i large) is occupied by a preceding segment of the same chain. Huggins estimated that f_0 should have a value of the order of 0.05. Hence, z' will not differ very much from z. Since z is to be employed as a semi-arbitrary parameter, it will be permissible to replace z' with z in Eq. (4), which on series expansion then becomes

$$\Delta\bar{S}_1 = Rv_2\{1/x + v_2[1-2(1-1/x)/z]/2 + v_2^2[1-4(1-1/x)/z^2]/3 + \cdots\}. \quad (4')$$

When x is large no significant error is introduced by dropping higher terms in x; hence,

$$\Delta\bar{S}_1 = Rv_2\{1/x + v_2(1-2/z)/2 + v_2^2(1-4/z^2)/3 + \cdots\}. \quad (4'')$$

Miller[6] arrived at a partial molal entropy expression practically equivalent to (4) by applying the Bethe first-order approximation method.

Recently Orr[7] has taken into account the effect of a non-zero energy of interaction between neighboring solvent molecules and polymer segments on the thermodynamic functions for the solution. His equation for $\Delta\bar{S}_1$ consists of two terms.[10] The first of these is equivalent to Huggins' Eq. (4), with z' replaced by z. The second consists of a power series in $(2w/zRT)$ where w represents the energy of interaction. In the first and dominant term of the series this quantity occurs as the square. Hence, the departures from random local mixing caused by positive as well as negative heats of mixing *increase* the entropy of dilution according to Orr's results. In the more common case where $w>0$, corresponding to endothermic mixing, it is found (letting $z=6$) that when w is sufficiently large to make the second term in Orr's equation exceed about 10 percent of the first term (Eq. (4)), immiscibility is encountered owing to the magnitude attained by the *heat* of dilution. For physically realizable mixtures of polymer and solvent Orr's correction for non-random local order in general is well within other limitations on the above theories (cf. seq.). Equations (1) and (4'') will therefore be employed to represent the essential results of all theories previously derived from the lattice model.[11]

When x is large the influence of x on the partial molal entropy is appreciable only in dilute solutions. At high dilutions the $1/x$ term in each of the series expansion forms of the above equations becomes dominant, and at infinite dilution

$$(\Delta\bar{S}_1/v_2)_{v_2=0} = R/x, \quad (6)$$

which is a necessary result required of any acceptable thermodynamic function regardless of the model assumed for the mixture.

For the purpose of comparing experimental results with theory it is desirable to deduct the $1/x$ term from the above equations, since x is characteristic only of the particular polymer employed. Also, since partial molal entropy values cover such a wide range when all concentrations are to be included, for graphical representations it is preferable to employ a suitable function of the partial molal entropy rather than the partial molal entropy itself. For this purpose, therefore, we shall employ a "reduced partial molal entropy," or "*RPME*," defined as follows:

$$RPME = \Delta\bar{S}_1/v_2 - (\Delta\bar{S}_1/v_2)_0, \quad (7)$$

where $(\Delta\bar{S}_1/v_2)_0$ denotes the limiting value of the ratio at $v_2=0$. Substituting from Eq. (6)

$$RPME = \Delta\bar{S}_1/v_2 - R/x. \quad (7')$$

Substituting from Eq. (3)

$$RPME = -R[(1/v_2)\ln(1-v_2)+1], \quad (8)$$

or

$$RPME = R[v_2/2 + v_2^2/3 + v_2^3/4 \cdots]. \quad (8')$$

The Huggins expression (4), with z' replaced by z, yields

$$RPME = -R[(1/v_2)\ln(1-v_2) - (1-1/x)(z/2v_2)\ln(1-2v_2/z) + 1/x], \quad (9)$$

[10] See Eq. (26b) of reference 7.

[11] If z is made sufficiently large the Huggins, Miller, and Orr expressions reduce eventually to Eq. (3). This is evident from their series expansions. Contrary to statements occurring in Orr's paper, in the derivation of Eq. (3) z was not assumed to be infinite. Under the approximations there employed, z does not appear in the entropy of mixing expression; it occupies a prominent place in the entropy of disorientation function, however.

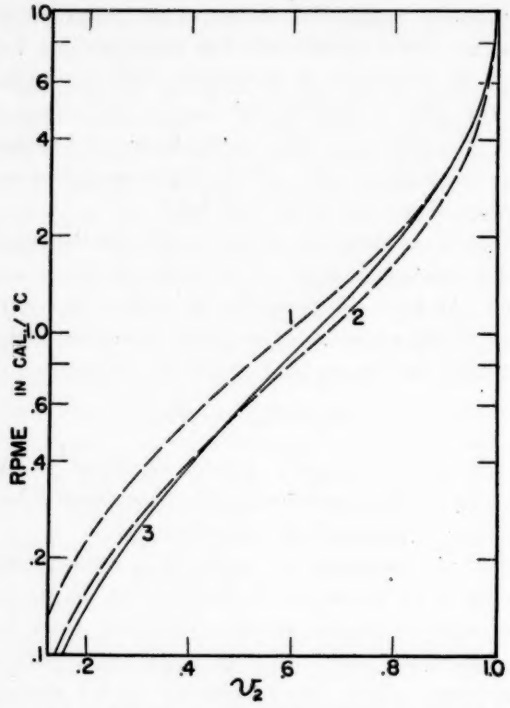

FIG. 1. Reduced partial molal entropy (log scale) *vs.* volume fraction of polymer for concentrated solutions. Curve 1, as calculated from (8); 2, as calculated from (9) with $z=6$; 3, experimental results for rubber in benzene.

which, in common with Miller's equation, can be expanded for large values of x to the form

$$RPME=R[v_2(1-2/z)/2 + v_2^2(1-4/z^2)/3+\cdots], \quad (9')$$

which again is independent of x.

COMPARISON OF CALCULATED AND OBSERVED PARTIAL MOLAL QUANTITIES

Entropies

The *RPME*'s calculated from Eq. (8) and from (9) with $z=6$ are plotted on a log scale against composition in Figs. 1 and 2. Experimental results of Gee and Treloar[12] on the rubber: benzene system are shown by the solid curves numbered "3" in each figure. This curve has been computed from the smoothed out partial molal entropies as given in Table VI of their paper, these being converted to calories per gram and substituted into Eq. (7). The R/x term, which is significant only at very low concentrations, has been obtained from extrapolation of their osmotic pressure results (cf. seq.). At high concentrations the agreement with Eq. (8), based on the writer's simpler Eqs. (1) and (3), is good; at intermediate concentrations the observed entropies depart from Eq. (8), but the *RPME* calculated from Eq. (9) with $z=6$ coincides with them fairly well; at low concentrations both calculated curves are too high. A smaller value of z would of course improve the fit at low concentrations, but only at the expense of the agreement reached at higher concentrations. Furthermore, a smaller coordination number would be unreasonable for the assumed lattice structure.

Thus, while either of Eqs. (8) or (9) has its merits at higher concentrations, neither appears to be satisfactory in dilute solutions. In the rubber: benzene system deviations from perfect random local order should be expected since the heat of mixing is appreciable, and positive. However, the resulting correction according to Orr's[7] treatment should not be large, and if applied would actually raise the calculated curve ($z=6$), thus increasing the discrepancy. The approximate estimate of this correction for dilute solutions published recently by Doty and Alfrey[13] likewise raises the theoretical curve farther from the observed results.

The logarithmic plots of Figs. 1 and 2 are unsatisfactory for very dilute solutions, i.e., in

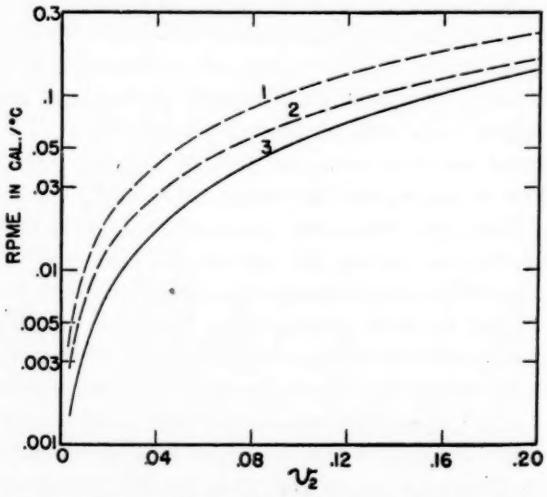

FIG. 2. Reduced partial molal entropy (log scale) *vs.* volume fraction of polymer for dilute solutions. Numeration of curves corresponds to Fig. 1.

[12] G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

[13] P. M. Doty and T. Alfrey, J. Chem. Phys. **13**, 77 (1945).

the region where osmotic pressure methods are commonly employed. Here it is customary to plot an osmotic pressure:concentration ratio against concentration. In Fig. 3 the function $T(RPME)$ is plotted against concentration (v_2), this function being related to a "reduced osmotic pressure," and to the π/v_2 ratio, as follows:

$$\begin{aligned} T(RPME) &\equiv T[(\Delta\bar{S}_1/v_2)-(\Delta\bar{S}_1/v_2)_0] \\ &= -[(\Delta\bar{F}_1/v_2)-(\Delta\bar{F}_1/v_2)_0] \\ &\qquad +\Delta\bar{H}_1/v_2 \\ &= V_1[(\pi/v_2)-(\pi/v_2)_0]+\Delta\bar{H}_1/v_2, \quad (10) \end{aligned}$$

where π is the osmotic pressure and V_1 is the molar volume of the solvent. The first term on the right side of (10) will be referred to as the reduced osmotic pressure. As in Figs. 1 and 2, curves 1 and 2 of Fig. 3 represent $T(RPME)$'s calculated, respectively, from Eq. (8), or (8′), and Eq. (9), or (9′), with $z=6$.

Experimental results for the following four polymer:solvent pairs are shown in Fig. 3: rubber in benzene (Gee and Treloar[12]), rubber in toluene (Meyer, Wolff, and Boissonnas[14]),[15] polyisobutylene in cyclohexane (Flory[16]), and polystyrene in toluene (Schulz[17]).[18] These particular pairs have been selected because they represent cases where either the heat of dilution term has been estimated experimentally from temperature coefficients, or the chemical similarity of solvent and solute lead to the conclusion that the heat term must be very small.

For the purpose of computing the function expressed in Eq. (10), it has been necessary first of all to assign values to $(\pi/v_2)_0$. The precise form of the π/v_2 *vs.* v_2 extrapolation to zero concentration has been subject to controversy. Thus, Meyer[14] and co-workers draw a straight line.

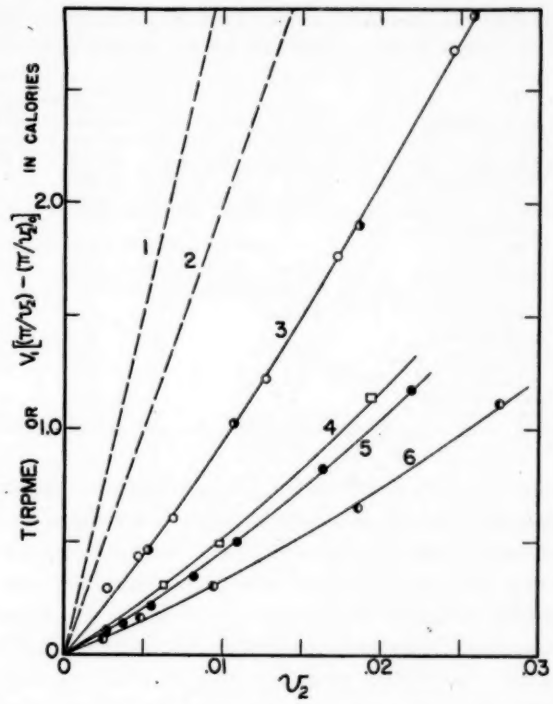

FIG. 3. $T(RPME)$, or the reduced osmotic pressure, *vs.* concentration in the very dilute region. Curve 1, $T(RPME)$ calculated from Eq. (8′); curve 2, calculated from Eq. (9′) with $z=6$. Curve 3, $T(RPME)$ for rubber in toluene (Gee and Treloar, see reference 12): ○ 55/45 fraction, ◑ intermediate fraction. Curve 4, □ reduced osmotic pressures for rubber in toluene (Meyer, Wolff, and Boissonnas, see reference 17). Curve 5, ● reduced osmotic pressures for polyisobutylene in cyclohexane (Flory, see reference 16). Curve 6, ◐ reduced osmotic pressures for polystyrene in toluene (Schulz, see reference 17).

Mark and co-workers[18] find the relationship to be linear when the polystyrene has been prepared above 100°, but curved upwards when prepared at 60°C. Schulz[17] used his specific co-volume equation which leads to opposite curvature at very low concentrations. Gee and Treloar[12] and the writer[16] find upward curvature.

For present purposes the various experimental π/v_2 values were re-plotted against v_2, and curves were drawn through the points with an admitted predisposition favoring the postulate that the curves for all of these solutions, when experimental errors are properly eliminated, should possess similar shapes. Since the balance of the evidence favors upward curvature, all have been drawn in this fashion. The limiting values of π/v_2 obtained in this way are given in Table I, where they are compared with the author's values. The corresponding molecular weights computed from

[14] K. H. Meyer, E. Wolff, and C. G. Boissonnas, Helv. Chim. Acta **23**, 430 (1940).

[15] H. Staudinger and K. Fischer, J. prakt. Chem. **157**, 19 (1940), obtained osmotic results for toluene solutions of rubber which agree with, but apparently are less accurate than, those of Meyer and co-workers.

[16] P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943).

[17] G. V. Schulz, Zeits. f. physik. Chemie **A176**, 317 (1936).

[18] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943), carried out more extensive osmotic pressure measurements on dilute solutions of polystyrene in toluene. While their results for the dependence of π/v_2 on concentration are generally similar to those of Schulz, they concluded that the shape and slope of the π/v_2 *vs.* v_2 curve depended somewhat on the temperature of preparation of the polymer. The set of data given here has been chosen arbitrarily from the work of Schulz.

TABLE I.

System	Source	Author's values $(\pi/v_2)_0$ atmos.	Author's values $V_1(\pi/v_2)_0$ cal.	Author's values $\bar{M}_n \times 10^{-5}$	Author's values α cal./mole	Values employed here $(\pi/v_2)_0$ atmos.	Values employed here $V_1(\pi/v_2)_0$ cal.	Values employed here $\bar{M}_n \times 10^{-5}$	Values employed here $\chi \times 10^{-3}$	Values employed here α cal./mole
Rubber: benzene (55/45 fraction)	Gee and Treloar[12]	0.148	0.321	1.5		0.100	0.217	2.2	2.75	58
Rubber: benzene (Intermediate fraction)	Gee and Treloar[12]	.080	.173	2.8	58±15	.050	.108	4.4	5.50	58
Rubber: toluene	Meyer, Wolff, and Boissonnas[14]	.082	.212	2.7	20±10	.105	.27	2.1	2.2	Neglected
Polyisobutylene: cyclohexane	Flory[16]	See Table II of reference 15								0
Polystyrene: toluene (Fraction II, prepared at 135°)	Schulz[17]	.115	.30	2.2	—	.127	.33	2.0	1.9	0

these $(\pi/v_2)_0$'s are also given. The curvature assigned to these plots is less than Gee and Treloar assumed at very low concentrations; hence our $(\pi/v_2)_0$'s are lower, and average molecular weights are higher, than theirs. In other cases assignment of upward curvature has raised $(\pi/v_2)_0$ somewhat, thus lowering $\bar{N}_n$. The precise value of $(\pi/v_2)_0$ is only of secondary importance here; a change in its value would merely shift the ordinate for each point of a given set in Fig. 3 by the same amount.

Except in the case of the rubber in benzene results, the quantity $V_1[(\pi/v_2)-(\pi/v_2)_0]$, obtained by deducting the $(\pi/v_2)_0$ values of Table I from observed (π/v_2)'s, is plotted directly in Fig. 3. In other words the $\Delta\bar{H}_1/v_2$ term of Eq. (10) has been neglected. Hence, curves 4, 5, and 6 are representative of the conventional π/v_2 *vs.* v_2 plots except that $(\pi/v_2)_0$ has been deducted from each ordinate, bringing the intercepts for all curves to the origin. This neglect of $\Delta\bar{H}_1$ assuredly is well justified for the polyisobutylene-cyclohexane and the polystyrene-toluene solutions, in consideration of the equivalence of cohesive energies of solvent and solute for each pair. Measurements of the temperature coefficient of osmotic pressures of rubber: toluene solutions by Meyer and co-workers[14] yield approximate heats of dilution, which when substituted in the van Laar expression

$$\Delta\bar{H}_1 = \alpha v_2^2, \tag{11}$$

lead to an α which is roughly equal to 20 cal. per mole (see Table I). If the $\Delta\bar{H}_1/v_2$ term of Eq. (10) had been included, with $\Delta\bar{H}_1 = 20v_2^2$, curve 4 would have been raised to a position between curves 3 and that now occupied by curve 4.

Results of Wolff[19] and of Staudinger and Fischer[15] on dilute solutions of gutta-percha in toluene agree in placing the reduced osmotic pressure curve very slightly above curve 4 of Fig. 3. Gutta-percha, being a configurational isomer of rubber hydrocarbon, would be expected to mix with toluene with the same heat effect. However, Wolff[19] concluded from the temperature coefficients of the osmotic pressure that the heat of mixing is approximately zero; i.e., $\alpha = 0 \pm 10$ cal. Hence, the $T(RPME)$ curve for gutta-percha is indicated to lie close to curve 4. The difference between the indicated values of α for rubber and for gutta-percha in toluene is not beyond the combined experimental errors, and it is possible that the $T(RPME)$ curves for both isomeric polymers lie near curve 4, or at any rate not far above it.[20]

The points along curve 3 of Fig. 3, depicting Gee and Treloar's[12] osmotic pressure results for rubber in benzene, represent $T(RPME)$'s computed in accordance with (10) from observed reduced osmotic pressures and a heat term calculated from the value of α (Table I) indicated by the temperature coefficient of osmotic pressure. Considering the experimental error in these

[19] E. Wolff, Helv. Chim. Acta **23**, 439 (1940).

[20] According to the results of Staudinger and Fischer (see reference 15), the π/v_2 *vs.* v_2 curves for toluene solutions of a series of polybutadienes ranging from 54,000 to 440,000 in molecular weight are substantially parallel. When $(\pi/v_2)_0$ values are deducted, these results fall very near to curve 4 of Fig. 3. If the reasonable assumption is made that the heat of dilution is negligible, curve 4 can be considered to represent $T(RPME)$ for the polybutadiene: toluene system also.

heats of dilution it is evident that the position of curve 3 for rubber:benzene is subject to at least as much uncertainty as are curves 5 and 6 for polyisobutylene:cyclohexane and polystyrene: toluene where no experimental estimates of α are available, but where chemical similarity of solvent and solute leads to the expectation of an α very nearly zero.

The most striking feature of Fig. 3 is the decidedly lower slopes of the experimental curves as compared with those calculated from theory. Comparing initial slopes, that for the rubber:benzene curve 3 is less than half the slope of calculated curve 2 ($z=6$); the other slopes are from four to six times lower than this calculated slope. To bring about approximate agreement between Eq. (9′) and curve 3 it would be necessary to reduce z to a value less than three; for the other solutions z would have to assume values less than 2.5. A lattice coordination number so low is inconceivable. If a value of this magnitude is accepted, the basic concept of a lattice composed of an array of cells is undermined.

The apparent curvature of these plots is also a significant, though much less disturbing, discrepancy. The above theory predicts a relationship which is very nearly linear, aside from the minor contribution of higher terms in the series expansion (see Eqs. (8′) and (9′)).

Heats of Dilution

If it is assumed that only interactions between nearest neighbors are important, then, as Orr[7] has shown most convincingly, the lattice theory leads to a heat of mixing of the van Laar form. The partial molal heat of dilution, consequently, should conform with Eq. (11). Gee and Treloar[12] found, however, that the observed partial molal heats of dilution could not be reconciled with (11) at all concentrations. Their values of $\Delta\bar{H}_1$, and the α's calculated from them, are given in Table II. Although the uncertainty in any single determination is relatively large, a much greater discrepancy between the indicated α's for low and for high concentrations is well established by these results.

Partial Molal Free Energies

Combining the lattice theory Eqs. (4) and (11) for the partial molal entropy and heat of dilution, respectively, there is obtained for the partial molal free energy

$$\Delta\bar{F}_1=RT[\ln(1-v_2)-(1-1/x)(z/2)\ln(1-2v_2/z)]+\alpha v_2^2.$$

Expanding the second logarithm in series and discarding terms beyond the second, Huggins[4] simplified this equation to

$$\Delta\bar{F}_1=RT[\ln(1-v_2)-(1-1/x)v_2+\mu v_2^2], \quad (12)$$

where

$$\mu=1/z+\alpha/RT. \quad (13)$$

Equation (12) is also obtained directly from Eqs. (3) and (11), except that μ is then to be redefined omitting the $1/z$ term of (13).

Huggins[4,21–23] has shown that published data on solutions of high polymers agree quite well with Eq. (12) when suitable values of μ are chosen. Only in the case of the rubber:benzene solutions do the available data extend beyond the dilute, or moderately dilute, region. The partial molal free energies[12] of benzene in this system for $v_2>0.02$ lead to μ values of 0.40 ± 0.03, the variation being not greater than the probable experimental error. At very low concentrations ($v_2<0.02$), an increase in μ is indicated by the experimental data.[24] The above value of μ is very nearly equal to α/RT at high concentrations (see Table II), the contribution of $1/z$ in Eq. (13) being negligible. This is merely a reiteration of the previously noted agreement of the simpler

TABLE II. Heats of dilution for rubber:benzene solutions. (From Gee and Treloar.[12])

v_2	$\Delta\bar{H}_1$ (cal./mole)	α
0.0127	$1.25\ (\pm0.6)\times10^{-2}$	78
0.0172	$1.8\ (\pm0.4)\times10^{-2}$	61
0.0210	$2.3\ (\pm0.8)\times10^{-2}$	52
0.0245	$3.1\ (\pm1.5)\times10^{-2}$	52
0.77	150 (±80)	250
0.915	190 (±80)	230
0.95	210 (±80)	230
0.99 to 1.00	390 (±80)	390

[21] M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942); Ann. N. Y. Acad. Sci. **44**, 431 (1943).
[22] M. L. Huggins, Ind. Eng. Chem. **35**, 216 (1943).
[23] M. L. Huggins, Ind. Eng. Chem. **35**, 980 (1943).
[24] It is unnecessary to include here a detailed analysis of the agreement between Eq. (12) and various sets of experimental results. This has been thoroughly covered by Huggins (see references 21, 22, and 23). See in particular Fig. 9 of reference 22.

theoretical Eq. (3) with experimental partial molal entropies at high concentrations. At lower concentrations α diminishes, according to the results quoted in Table II, but μ remains approximately constant. Hence, it is necessary to re-formulate μ as follows:

$$\mu=\beta+\alpha/RT, \tag{14}$$

where β is an empirical quantity which, in common with α, varies with composition; α retains the definition inherent in Eq. (11). Thus, in spite of the failure of both the theoretical entropy and heat functions separately, when combined in the free energy function a surprisingly close approximation to the observed results for rubber in benzene is obtained. This agreement is attained, however, by assigning to μ an arbitrary value which at lower concentrations does not accord with the theoretically derived μ of Eq. (13).

In other polymer:solvent systems it is likewise necessary to throw the burden of μ on β in dilute solutions. If the mixture is more nearly athermal than the rubber:benzene solution, α will be small at all concentrations, and a marked decrease in μ with increasing concentration can be expected. Further experimental data covering a wide range of concentrations are needed to clarify this point.

A NEW THEORY FOR DILUTE SOLUTIONS

In the derivation of Eq. (3) it was assumed[5] that, with respect to any given polymer molecule to be added to the lattice, those previously added occupy a random distribution of occupied sites. In Huggins' derivation[4] of Eq. (4) this random distribution was appropriately modified only insofar as immediate lattice neighbors are concerned (see (b) on page 454). That is, in seeking the number of available sequences of x sites in the lattice which remain vacant and hence could be occupied by the molecule in question, it has been assumed that segments of the molecules previously added are distributed essentially at random, rather than in continuous sequences of x consecutively adjacent cells. In sufficiently concentrated solutions the molecules will be intertwined to such an extent that no long range departures from this assumed random distribution of occupied sites are to be expected. Hence, the above assumption, inherent in the theories examined above, should be inconsequential here.

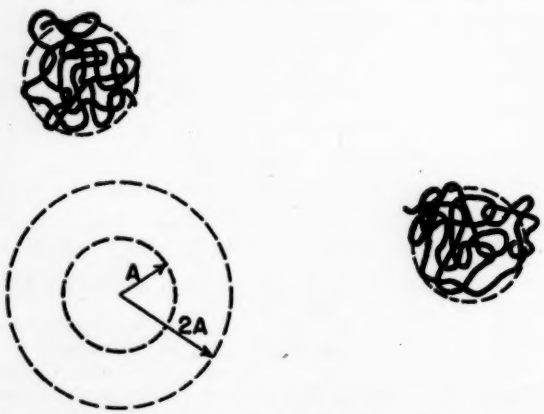

FIG. 4. Diagrammatic representation of an extremely dilute solution of an irregularly coiled long chain polymer.

In very dilute solutions this assumption is totally invalid for solutes composed of very long (large x) flexible molecules. Each polymer molecule occupies a sequence of x sites in the same locality. Between these regions all sites are vacant. The very dilute solution, therefore, consists of two regions, one completely unoccupied by solute and the other possessing an average "concentration" of occupied sites determined by the statistical configuration of the polymer chain and independent of the over-all average concentration of polymer. As the concentration is increased the extent of the former region is decreased and the latter is increased.

This concept of a dilute solution of randomly coiled polymer molecules is illustrated in Fig. 4. The actual domain pervaded by a polymer chain is not sharply defined. For the purpose of carrying out an approximate treatment, it will be assumed that each molecule is distributed within an effective volume of radius A. All molecules are assumed to be of the same size. As a convenient approximation it is assumed further that within the sphere of radius A the average concentration of polymer segments is radially uniform, i.e., independent of the distance from the center. Then if the swelling factor s is defined as the ratio of lattice cells within the sphere of radius A to the number x of polymer segments

$$(4/3)\pi A^3=sxV_1$$

where V_1 is the molecular volume of the solvent, the volume fraction of polymer within the sphere is $1/s$. For a large, randomly coiled

polymer molecule $1/s$ will be small—of the order of .05 or less.

It can be shown as follows that the molecules will tend to avoid overlapping in spite of the fact that the concentration of segments $1/s$ is small within the domain of radius A occupied by a molecule. The probability that an arbitrarily chosen sequence of j vacant sites ($j \leqq s$) exists within a sphere occupied by a molecule, and hence is available for occupancy by j segments of another molecule, is $(1-1/s)^j$. Although $1/s$ may be quite small, the above factor becomes small when j exceeds s. Since s is generally much smaller than x, it is clear that a considerable degree of overlapping, corresponding to a j value which is a considerable fraction of x, will be discouraged by the adverse statistical factor given above. Hence, to a first approximation the molecule will not overlap so long as unoccupied space is available elsewhere in the lattice. In the treatment which follows overlapping nevertheless is taken into account in an approximate manner.

If N polymer molecules have been added to the lattice previously, then the number of configurations, ν_{N+1}, available to the next molecule to be added can be expressed in two separate terms: the number ν'_{N+1} of available configurations in which the domain of the $(N+1)$th molecule does not overlap that of any other, and the ν''_{N+1} available configurations in which some degree of overlapping does occur. Each of the N molecules blocks out a volume of radius $2A$ in which the center of another molecule cannot be placed without encountering overlapping. The total volume blocked out by N molecules poses a difficult geometrical problem owing to the fact that the regions distant A to $2A$ from the centers of different molecules may overlap freely. Here we neglect this factor and simply express the volume (more accurately, the number of lattice cells) which the center of the $(N+1)$th molecule may not enter without introducing overlapping of its domain (radius A) with that of another previously added molecule as

$$4\pi(2A)^3N/3 = 8sxN. \qquad (15)^{25}$$

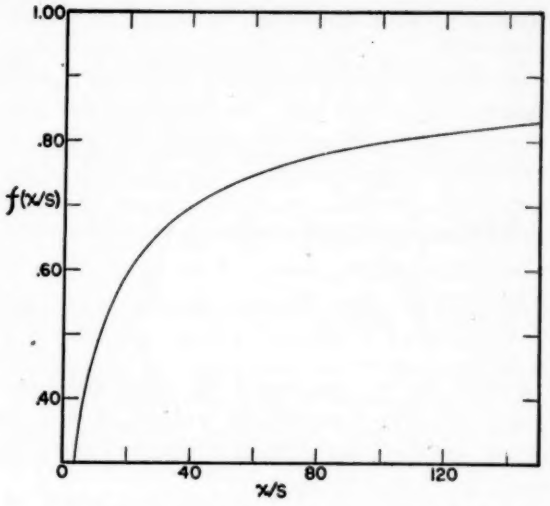

FIG. 5. The function $f(x/s)$ as computed from (19).

Since there will be $n_0 - 8sxN$ lattice sites available to the center of the $(N+1)$th molecule such that no overlapping will occur,

$$\nu'_{N+1} = (n_0 - 8sxN)(z-1)^{x-1}. \qquad (16)^{26}$$

If the center of the $(N+1)$th molecule falls on one of the $8sxN$ (according to the above assumption) lattice sites which lies at a distance $a < 2A$ from the center of a previously added molecule, the two molecules will jointly occupy a volume

$$V_J = (sxV_1)(y^3 - 3y + 2)/2, \qquad (17)$$

where $y = a/2A$. Within this region of joint occupancy the expected number of sites available to each consecutive segment of the $(N+1)$th molecule is reduced to $(1-1/s)(z-1)$ owing to the concentration $1/s$ of segments of the other molecule; for segments falling outside this region the factor is of course $(z-1)$. Hence

$$\nu''_{N+1} = N \sum_{\substack{8sx \\ \text{cells}}} [(z-1)^{x-1}(1-1/s)^{(x-1)V_J/sxV_1}].$$

Replacing the summation by an integral and

[25] A somewhat better approximation probably is obtained by setting the blocked out volume equal to

$$8sxN[1 - q(1-q/8)sxN/n_0]$$

where q is the ratio of the total volume to the actual volume of close packed, non-interpenetrating spheres. Thus, when the concentration of polymer is extremely small the above function is equivalent to (15). In contrast to (15), however, the blocked out volume according to this expression does not reach the total volume, represented by the total number of cells n_0, until $sxN = n_0/q$. The value of q should be 1.35 to 2.0.

Substitution of this expression in place of Eq. (15) does not appear to alter the essential character of the results obtained. Only the second and higher terms of the series in Eq. (22′) are lowered somewhat.

[26] The symmetry factor, ½, to account for the twofold symmetry of the linear polymer molecule is here omitted.

substituting from Eq. (17)

$$\nu''_{N+1}=8sxN(z-1)^{x-1}[1-f(x/s)], \quad (18)$$

where

$$f(x/s)=1-\int_0^1 (1-1/s)^{(x-1)(y^3-3y+2)/2}3y^2dy$$

which for large values of s reduces, approximately, to

$$f(x/s)=1-\int_0^1 [\exp\,(-x/2s)]^{(y^3-3y+2)}3y^2dy. \quad (19)$$

In Fig. 5 $f(x/s)$, computed by graphical integration of (19) for various values of x/s, is plotted against x/s. An asymptotic increase toward unity is indicated.

Combining Eqs. (16) and (18)

$$\nu_{N+1}=\nu'_{N+1}+\nu''_{N+1}=(z-1)^{x-1}(n_0-gxN), \quad (20)$$

where $g=8sf(x/s)$. The total number of configurations for N polymer molecules in the lattice composed of n_0 cells is given by

$$W=(1/N!)\prod_{N=1}^{N}\nu_N$$

$$=(1/N!)(gx)^N(z-1)^{N(x-1)}\prod_{N=1}^{N}\left[\frac{n_0}{gx}-(N-1)\right]$$

$$=(1/N!)(gx)^N(z-1)^{N(x-1)}$$

$$\times(n_0/gx)!/[(n_0/gx)-N]!.$$

Introducing the Boltzmann relationship $\Delta S/R=\ln W$ and replacing factorial terms with their Stirling approximations

$$\Delta S/R=N[\ln\,(gx/N)+(x-1)\ln\,(z-1)]$$
$$+(n_0/gx)\ln\,(n_0/gx)$$
$$-[(n_0/gx)-N]\ln[(n_0/gx)-N]. \quad (21)$$

If n_0 is replaced by its equivalent $n+xN$ in the above expression for the entropy of mixing, which is then differentiated with respect to n, there is obtained for the partial molal free energy

$$\Delta\bar{S}_1/R=-(1/gx)\ln[1-gxN/(n+xN)]$$
$$=-(1/gx)\ln\,(1-gv_2) \quad (22)$$

$$=v_2[1/x+(4sf/x)v_2$$
$$+(64s^2f^2/3x)v_2^2+\cdots]. \quad (22')$$

In the series expression (22′) g has been replaced by $8sf$, with f representing $f(x/s)$. When the heat of mixing can be neglected, the reduced osmotic pressure function becomes

$$V_1[(\pi/v_2)-(\pi/v_2)_0]=T(RPME)$$
$$=RT[(4sf/x)v_2+(64s^2f^2/3x)v_2^2+\cdots]. \quad (23)$$

From Eq. (22) it is clear that the present treatment is limited to concentrations such that gv_2 is considerably less than unity, i.e., to dilutions such that only a small fraction of the volume is encompassed by the randomly coiled molecules. Hence, the treatment is essentially limited to the range where higher terms of Eq. (22′) are small compared to the first. For athermal solutions this corresponds to the region where π/v_2 is only fractionally greater than $(\pi/v_2)_0$. Here we shall be concerned only with the second term of Eq. (22′), or the first term of Eq. (23), which predicts the initial slope for a π/v_2 *vs.* v_2 plot, or for a plot such as the one shown in Fig. 3. In consideration of the approximate nature of the theory on the one hand and the experimental difficulties attending accurate determination of the shape of the π/v_2 *vs.* v_2 plot in the very dilute region, higher terms will be disregarded.[27]

COMPARISON OF THE NEW THEORY FOR DILUTE SOLUTIONS WITH EXPERIMENT

Dilute Solutions of Irregularly Coiled Long Chain Polymers

A test of the above equations requires an independent estimate of s, the ratio of the effective to the actual molecular volume. According to Kuhn's[28] interpretation of viscosities in dilute polymer solutions, it is possible to estimate an effective volume for the dissolved polymer molecule from the viscosity increment, or intrinsic viscosity, of the solution. Kuhn considers that when the chain length is great[29] solvent within the region occupied by the randomly coiled molecule moves with the molecule as a unit. If the rate of shear is not too great, the molecule plus "enclosed" solvent affects the viscosity in much

[27] When the somewhat better approximation mentioned in footnote 25 is employed, the first and second term of the series expansion obtained for $\Delta\bar{S}_1/R$ are identical with those of Eq. (22′), while higher terms are reduced. The range of convergence is therefore extended to higher concentrations. This suggests that the first two terms of Eq. (22′) may be valid over a somewhat greater concentration range than the above equations alone would indicate.

[28] W. Kuhn, Kolloid Zeits. **58**, 2 (1934); **49**, 959 (1936).

[29] W. Kuhn and H. Kuhn, Helv. Chim. Acta **26**, 1394 (1943).

TABLE III. Comparison of observed initial slopes for the $V_1(\pi/v_2)$ *vs.* v_2 curve with those calculated from the theory for dilute solutions.

Polymer designation	Polyisobutylene in cyclohexane[15] B (9–13)	Polyisobutylene in cyclohexane[15] C (4–9)	Polystyrene in toluene;[17] 135° polymer fraction II
$\bar{M}_n$	78,000	256,000	200,000
x	780	2560	2000
$[\eta]$	0.70*	1.45*	1.03
s from Eq. (24)	26	54	43
x/s	30	47.5	46.5
$f(x/s)$ from Fig. 5	0.66	0.72	0.72
Slope calc'd. $RT(4sf/x)$, cal.	53	36	37
Observed slope, cal.	38	38	31

* The intrinsic viscosities of these samples were not published; the above intrinsic viscosities have been calculated from their molecular weights and the known intrinsic viscosity-molecular weight relationship *in cyclohexane.*

the same way as would a suspended rigid sphere. Then, according to Einstein's equation

$$\eta_r - 1 = 2.5 v_2',$$

where η_r is the relative viscosity and v_2' is the volume fraction of suspended spheres. Setting $v_2' = sv_2$

$$(\eta_r - 1) = 2.5 s v_2$$

and converting to intrinsic viscosity

$$[\eta] \equiv [(\eta_r - 1)/c]_{c=0} = 0.025 s/\rho, \qquad (24)$$

where c is the concentration of polymer in g. per 100 ml and ρ is the density of the polymer. The value of s computed from the intrinsic viscosity using Eq. (24) may not, of course, necessarily correspond to the effective volume ratio of concern here; the former is a kinetically determined quantity while the latter relates to an equilibrium property. Presumably these effective volumes should at least be similar in magnitude, however.

In Table III several examples are given to illustrate the calculation of the π/v_2 *vs.* v_2 slope term, $4RTsf/x$ according to (23), from the "viscosity" s value. The calculated slopes are in remarkably good agreement with those observed. The differences are scarcely greater than the experimental error on the one hand, and on the other they are well within the limits imposed by the approximations in the development of the theory.

The slope term calculated as above is found to decrease slowly with increase in molecular weight. This can be shown as follows. Since s is proportional to the intrinsic viscosity and the intrinsic viscosity generally depends on about the two-thirds power of the molecular weight[16] (i.e., $x^{\frac{2}{3}}$), x/s should vary approximately as $x^{\frac{1}{3}}$. In the slope term, $4fs/x$, the change in x/s with x is partially, but not entirely, offset by the increase in f with x/s (see Fig. 5). The net predicted decrease in slope of the π/v_2 *vs.* v_2 plot with molecular weight is quite small, and, in view of the approximate nature of the theory, may not necessarily be significant. Nevertheless Gee and Treloar[12] have reported a decrease in the slope with molecular weight for the rubber:benzene system, in support of this prediction. The writer[16] failed to observe a change in initial slope with molecular weight for polyisobutylene in cyclohexane, perhaps owing to the failure to extend accurate osmotic pressure-concentration measurements over a sufficiently extended molecular weight range.

The Heat of Dilution in Dilute Solutions

If there were no overlapping of the regions occupied by the polymer molecules there would be virtually no heat change on dilution with additional solvent; $\Delta\bar{H}_1$ would equal zero in the very dilute solution regardless of the nature of the interactions between like and unlike components. Actually some overlapping will occur, and its extent presumably will vary in proportion to the concentration. Where overlapping occurs the number of polymer-to-polymer contacts will be increased while the number of solvent-to-polymer contacts are decreased. Hence, the heat of mixing should assume the form

$$\Delta H = \Delta H_0 - (\text{const.}) \times v_2,$$

where ΔH_0 is the heat of mixing N polymer molecules with an infinite amount of solvent. Upon differentiating with respect to moles of solvent, an expression of the van Laar form, Eq. (11), is obtained for the partial molal heat of dilution. When the concentration is so increased that the molecules necessarily overlap extensively, this derivation no longer holds. Eventually at high polymer concentrations the proportion of polymer:polymer contacts, as compared to polymer:solvent contacts, will approximate that

prevailing in a solution of a monomeric analog of the polymer at the same volume concentration. Here the heat of dilution for the polymer solution may again be expected to follow the van Laar formula, but with a different value of α.

It is also evident from the above discussion that the proportion of polymer-to-polymer contacts in a dilute polymer solution will be much less dependent on concentration, and hence $\Delta\bar{H}_1$ will be smaller in magnitude, than in the case of a solution containing a monomeric solvent at the same actual volume concentration. Consequently, α should be correspondingly much smaller in dilute polymer solutions. In more concentrated solutions it should assume a value more nearly that to be expected for random mixing of a monomeric solute with solvent. Thus, the large change in the apparent α's in passing from dilute to concentrated solutions of rubber in benzene[12] (see Table II) is readily explained in the light of the discontinuous character of dilute polymer solutions.

Compact Polymer Molecules (Proteins) in Solution

Results obtained with the ultracentrifuge show that protein molecules are "globular" in solution. In contrast with synthetic high polymers, rubber and cellulose derivatives, the native protein molecules assume a definite, fairly compact form in solution, not highly swollen by solvent (water). Their intrinic viscosities are small—around 0.05—in harmony with this conclusion. Hence, s should be small, having a value from one to not over three at the most.

When s is small Eq. (22), or (22′), predicts only a very gradual departure from van't Hoff's law with increasing concentration. This is actually observed to be the case for solutions of undenatured proteins near their isoelectric points.[30,31] In fact, by suitably choosing s values in the range from one to two, the observed osmotic pressures[31] of hemoglobin, serum albumin, myogen, and casein are well duplicated by Eq. (22), or (23), up to concentrations of ten or twenty percent. These values of s are precisely in the range to be expected according to the known character of the protein solute. Denaturation, which is believed to involve unfolding of the polypeptide chain, is accompanied both by an increase in intrinsic viscosity and by an increase in the departure from van't Hoff's law,[31] both corresponding to an increase in s.

Although native protein molecules generally are somewhat ellipsoidal, those mentioned above probably do not depart from sphericity sufficiently to invalidate correlation with the theory here developed. Thus, the character of the deviation from van't Hoff's law can be used as a criterion of the nature of the dissolved protein particle.

Thermodynamics of Highly Swollen Gels

Insoluble polymers having a loose network structure (e.g., a very lightly vulcanized rubber) will swell in suitable solvents to the extent that they become dilute polymer "solutions," although they will not disperse as solutions in the ordinary sense. With low degrees of cross-linking, or branching, the gel at equilibrium with excess solvent may contain no more than two percent polymer. Owing to the permanence of the network structure, the polymer chains are prevented from segregating from one another entirely. Hence, the discontinuities of the dilute polymer solutions previously discussed will be suppressed, although not necessarily entirely eliminated, in swollen network gels. The theories developed previously perhaps may be more appropriately applied to swollen gels[32] than to finite (soluble) polymers. In support of this view a value of μ equal to about 0.3 has been indicated for vulcanized butyl rubber (essentially cross-linked polyisobutylene) swollen in cyclohexane;[33] for soluble polyisobutylene in the same solvent[16] $\mu=0.41$.[23]

SUMMARY AND CONCLUSIONS

Previous statistical mechanical treatments of polymer solutions have been compared. All of them stem from similar concepts regarding the

[30] See for example the results of G. S. Adair, Proc. Roy. Soc. 120A, 573 (1928), on osmotic pressures of aqueous hemoblobin.

[31] For a summary including other proteins, see *The Chemistry of Amino Acids and Proteins*, edited by C. L. A. Schmidt (C. C. Thomas, Publishers, Springfield, Illinois, 1944), Chapter VIII by D. M. Greenberg.

[32] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 521 (1943).

[33] P. J. Flory, Chem. Rev. 35, 51 (1944).

physical constitution of solutions of long chain molecules; their results consequently are similar. While they predict partial molal entropies in good agreement with observations at high concentrations of polymer, large discrepancies are noted in dilute solutions; the predicted deviations from Raoult's law are several-fold too large at concentrations of several percent or less.

The assumption of random occupancy of lattice sites by polymer sements, which is inherently a part of the previous treatments of polymer solution statistical mechanics, has been shown to be at fault at high dilutions. Here the solution is decidedly discontinuous. Loose clusters of segments, corresponding to individual polymer molecules, occupy separate regions of the volume. Between them the medium consists of pure solvent.

A new theory based on this concept has been developed. The deviation from ideality is found to be a function of the "effective volume ratio" or "swelling factor" s, which represents the ratio of the volume of the solution pervaded by a polymer molecule to its actual molecular volume. For a long, flexible chain molecule in solution, s will be large; it can be estimated from the intrinsic viscosity. Initial slopes of the π/v_2 (osmotic pressure: concentration ratio) *vs.* v_2 plots for hydocarbon polymers in non-polar solvents calculated from "viscosity" s values in accordance with the new theory for dilute solutions are in remarkably good agreement with experiment. The theory also predicts a very small decrease in this slope with increase in molecular weight.

Solutions of native proteins deviate very slowly from van't Hoff's law with increase in concentration. This is to be expected according to the present theory, owing to the compact form of the protein molecule in solution. Hence a new method for characterizing the form of the protein molecule in solution is suggested. Existing data for proteins such as hemoglobin and serum albumin indicate s values in aqueous solutions between one and two.

The segregation which exists in dilute solutions also affects the partial molal heat of dilution $\Delta\bar{H}_1$. In dilute solutions $\Delta\bar{H}_1$ is smaller than would be the case for random mixing of the separate segments. A single van Laar heat of mixing expression will not hold for all concentrations.

Unfortunately, the present treatment of entropies of mixing is limited (except for compact solutes such as proteins) to extremely dilute solutions ($sv_2 \ll 1$), and no means for integrating it with the previous theories applicable at higher concentrations is yet apparent. It is obvious, however, that discontinuties in polymer segment occupancy of the cells of the liquid lattice will persist well beyond the concentration at which polymer molecules encompass almost the entire volume (which may occur at concentrations of several percent, depending of course on the intrinsic viscosity). Eventually these discontinuties virtually disappear as the concentration is further increased. At concentrations beyond 20 to 30 percent polymer the previous theories give a reasonably good account of the facts.

Various attempts at improvement of the mathematical exactness of these previous theories have been published[6–8] recently. However, in the opinion of the writer it is doubtful that the assumptions inherent in the idealized lattice model warrant these refinements. The simpler theoretical treatment[5] by means of which the relatively tractable entropy of mixing expression (1) was derived is well within the bounds of these physical approximations in the assumed model.[34]

In spite of the divergence in dilute solutions from the previously derived partial molal entropy and heat of dilution expressions, when these are combined a free energy function is obtained which, as Huggins[21–23] has shown, is empirically acceptable through the dilute solution range, and in one instance (rubber in benzene) at all concentrations. The present work serves to clarify to some extent the semi-empirical character of the single parameter μ contained in this free energy function. In spite of the approximate constancy of μ for rubber in benzene at all concentrations, it is unlikely that this condition applies to high polymer solutions generally.

[34] See also P. J. Flory, J. Chem. Phys. 12, 425 (1944).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 11 NOVEMBER, 1945

The Variation of the Transference Numbers for Calcium Chloride in Aqueous Solution with Temperature. III

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(Received August 2, 1945)

Transference numbers for calcium chloride in aqueous solution have been determined for concentrations up to 0.15N at 15°, 25°, and 35°C. At all three temperatures autogenic cation boundaries using cadmium chloride as indicator gave transference numbers which showed no progression as the boundary moved and were independent of current. The same was true of anion boundaries (employing calcium iodate and paratoluene sulphonate as indicators) at 25°C provided the concentrations of the indicator ions were held within rather narrow limits. Where both t_+ and t_- were determined for a solution, their sum was unity within the precision of the measurements. These results differ, however, from Longsworth's data by somewhat more than the apparent precision of the measurements. The variation of the transference numbers with temperature is normal in that they tend to approach one-half with increasing temperature. As in the case of sodium chloride, the variation of the transference number with concentration is independent of the temperature.

PREVIOUS papers from this laboratory[1,2] have reported the temperature coefficients for the transference numbers of potassium and sodium chlorides; the work described here was originally undertaken several years ago to provide similar information for calcium chloride —a typical 2:1 electrolyte.

The experimental technique was the same as that previously used; the majority of the data were obtained with autogenic boundaries (cell II) using cadmium chloride as a cation indicator, but a considerable number of runs at 25° were made with sheared boundaries (cell III) employing calcium iodate and calcium paratoluene sulphonate as anion indicators; both these indicators of course give rise to ascending boundaries. In the case of the autogenic cation boundaries, no progression was ever observed in the measured transference number as the boundary moved up the tube. In all cases the current was varied by a factor of 2 from run to run for a given round concentration, and the measured t_+ was invariably independent of the current within the precision of the measurements. In this respect the behavior of calcium chloride resembles that of potassium chloride and of sodium chloride rather than that of potassium bromide.[3]

For anion boundaries, the use of calcium iodate as indicator is restricted, owing to its low solubility, to calcium chloride solutions 0.02N or less. At 0.01N and 0.02N, however, iodate boundaries show no progression and are independent of the current if the indicator concentrations are 0.00595N and 0.0120N, respectively; it might be noted that these are approximately the concentrations predicted by the Kohlrausch rule.[4] The same is true for indicator concentrations differing from these values by not more than 1 percent; beyond these ranges however, the measured t_- was lower, and while showing no progression, depended on the current.

With paratoluene sulphonate as indicator, transference numbers showing no progression and independent of current were obtained with indicator concentrations of 0.0103 and 0.0280N for 0.02N and 0.05N calcium chloride, respectively. Here again, the indicator concentrations were critical to about 1 percent; beyond this range, the measured t_- were high and varied with the current used, although showing no progression. Since the values obtained at 0.02N and 0.05N for t_- were in good agreement with

* Canadian Industries Limited Fellow in Chemistry, 1943–1944.

[1] R. W. Allgood, D. J. LeRoy, and A. R. Gordon, J. Chem. Phys. 8, 418 (1940).

[2] R. W. Allgood and A. R. Gordon, J. Chem. Phys. 10, 124 (1942).

[3] A. G. Keenan and A. R. Gordon, J. Chem. Phys. 11, 172 (1943).

[4] D. A. MacInnes and L. G. Longsworth, Chem. Rev. 11, 171 (1932).

TABLE I.

Cell	Conc.	$t_\pm$ obs.	Sol.+Vol. Corr.	$t_\pm$
		15° Centigrade		
II	0.019990	0.4190	+0.0002	0.4192
II	0.019990	0.4189	+0.0002	0.4191
II	0.019995	0.4188	+0.0002	0.4190
II	0.029980	0.4153	+0.0001	0.4154
II	0.029970	0.4155	+0.0001	0.4156
II	0.05002	0.4104	0.0000	0.4104
II	0.05006	0.4101	0.0000	0.4101
II	0.05006	0.4101	0.0000	0.4101
II	0.05006	0.4104	0.0000	0.4104
II	0.05029	0.4104	0.0000	0.4104
II	0.09987	0.4025	−0.0001	0.4024
II	0.09987	0.4022	−0.0001	0.4021
II	0.10004	0.4024	−0.0001	0.4023
II	0.14993	0.3967	−0.0002	0.3965
II	0.14993	0.3967	−0.0002	0.3965
II	0.15001	0.3968	−0.0002	0.3966
		25° Centigrade		
III, *i*	0.009997	0.5714	+0.0008	0.5722
III, *i*	0.009975	0.5712	+0.0008	0.5720
III, *i*	0.019972	0.5763	+0.0004	0.5767
III, *i*	0.019972	0.5765	+0.0004	0.5769
III, *p*	0.019995	0.5766	+0.0004	0.5770
III, *p*	0.019995	0.5762	+0.0004	0.5766
II	0.019997	0.4231	+0.0003	0.4234
II	0.020061	0.4232	+0.0003	0.4235
II	0.029919	0.4202	+0.0001	0.4203
II	0.029919	0.4200	+0.0001	0.4201
II	0.030065	0.4202	+0.0001	0.4203
II	0.049991	0.4150	0.0000	0.4150
II	0.049991	0.4151	0.0000	0.4151
II	0.050051	0.4150	0.0000	0.4150
III, *p*	0.050051	0.5847	+0.0003	0.5850
III, *p*	0.050051	0.5846	+0.0003	0.5849
II	0.06977	0.4117	−0.0001	0.4116
II	0.07001	0.4116	−0.0001	0.4115
II	0.09618	0.4078	−0.0001	0.4077
II	0.09714	0.4078	−0.0001	0.4077
II	0.09721	0.4074	−0.0001	0.4073
		25° Centigrade		
II	0.09985	0.4072	−0.0001	0.4071
II	0.14428	0.4020	−0.0003	0.4017
II	0.14997	0.4013	−0.0003	0.4010
II	0.15014	0.4015	−0.0003	0.4012
		35° Centigrade		
II	0.019999	0.4272	+0.0005	0.4277
II	0.020007	0.4274	+0.0005	0.4279
II	0.029967	0.4246	+0.0003	0.4249
II	0.029968	0.4242	+0.0003	0.4245
II	0.030030	0.4244	+0.0003	0.4247
II	0.049973	0.4198	0.0000	0.4198
II	0.049974	0.4200	0.0000	0.4200
II	0.049749	0.4201	0.0000	0.4201
II	0.050027	0.4198	0.0000	0.4198
II	0.09982	0.4119	−0.0002	0.4117
II	0.09982	0.4118	−0.0002	0.4116
II	0.09993	0.4120	−0.0002	0.4118
II	0.14983	0.4059	−0.0004	0.4055
II	0.14977	0.4061	−0.0004	0.4057

the corresponding values of t_+ determined in the autogenic cell, and since the autogenic measurements in all cases satisfied two of the criteria for a transference number (absence of progression and independence of current), it seemed justifiable to employ the autogenic cell for the 15° and 35° runs.

As Shedlovsky and Brown[5] have pointed out, the most serious difficulty in working with calcium chloride solutions is the preparation of a neutral solution of accurately known strength; we have followed essentially the procedure they recommend. B.D.H. "Analar" grade calcium chloride was crystallized twice from conductivity water; the crystals were collected on a Buchner funnel, and the residual moisture was allowed to distill off for several days into a dry ice trap under vacuum; the resulting material was practically anhydrous but slightly basic. A sample of the salt in a tared platinum boat was introduced into a silica tube electrically heated to 800°C, through which a stream of carefully dried nitrogen was passing. After the salt had melted, dry hydrogen chloride was passed over the melt for 10 minutes, and then nitrogen for a further 10 minutes; the boat was then pulled to the cold exit end of the tube, allowed to *cool* there in the nitrogen stream for 5 minutes, and then transferred to a stoppered weighing bottle, which after 30 minutes in a desiccator, was transferred to the balance case, and weighed after 10 minutes. Stock solutions were prepared gravimetrically from the fused salt and conductivity water; when tested by means of a Coleman or Beckman glass electrode, the *p*H of the resulting solution never differed by more than one or two tenth's of a *p*H unit from that of the conductivity water, *viz.* 5.8 to 6.2.

The necessity for having neutral solutions was demonstrated by some measurements in which the stock solutions, owing to an imperfect fusion, had a *p*H when first made up of approximately 9. Measurements at 0.01*N* and 0.02*N* with calcium iodate as anion indicator gave transference numbers which showed no progression and were independent of current but were approximately 0.25 percent too high, i.e., values of t_+ obtained from them would have been low by roughly 0.3 percent.

As a further check on the method of preparation, some of the stock solutions were analyzed gravimetrically for chloride. A weighed sample (approx. 80 cc) of the 0.5*N* stock was diluted to 200 cc with conductivity water.[6] The precipitation was carried out with a standardized 0.2*N* silver nitrate solution, the chloride solution being first inoculated with 3 cc of 0.05*N* silver nitrate; a slight excess of the fifth normal solution was then added slowly and with constant stirring in the cold until the final silver ion concentration was 0.05 grams per liter. The precipitate was allowed to stand for 15 hours in the dark, and the clear supernatant liquid was decanted through a

[5] T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. 56, 1066 (1934).

[6] Richards and Wells (J. Am. Chem. Soc. 27, 459 (1905)) have shown that occlusion in the precipitated silver chloride is negligible at concentrations 0.2*N* or less.

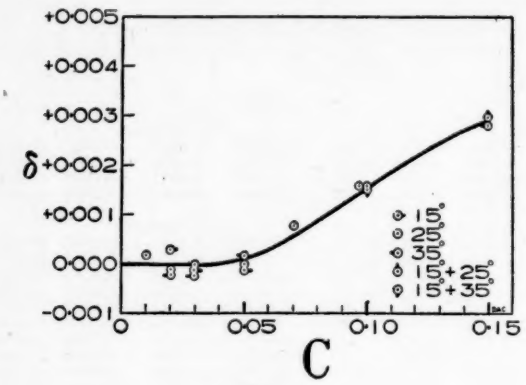

FIG. 1

tared Gooch crucible. The precipitate was vigorously washed with four 30-cc portions of 1 percent nitric acid, and was then transferred to the crucible, using about 200 cc of the acid for the transfer; it was finally washed in the crucible with three 10-cc samples of conductivity water, dried for 1 hour at 100°C and for 3 hours at 150°C, cooled for 45 minutes, and weighed. Duplicate analyses by this method under the conditions outlined above were carried out on 0.2*N* KCl and NaCl solutions prepared gravimetrically from samples of the recrystallized salts fused in platinum in an atmosphere of dry nitrogen;[1,2] in both cases the results were 0.015 ±0.002 percent too low. This small discrepancy was presumably due, in part at least, to the fact that no correction was applied for the trace of silver chloride dissolved in the washings. However, since the error is independent of the cation, it seemed permissible to apply a similar correction to the results of the calcium chloride analyses. When this is done, the resulting concentration of the calcium chloride solution agrees within 0.004 percent with that computed from the known weights of the salt and the water used in making it up. It therefore seems safe to assume that our concentrations are known to 0.01 percent or better. It should also be noted that at least two solutions, each prepared by gravimetric dilution of a different stock solution, were employed for a series of measurements at a given round concentration. In computing volume concentrations, all weights have been reduced to vacuum, and the density data in International Critical Tables[7] were employed.

[7] *International Critical Tables*, Vol. 3, p. 72. See also reference 5.

The calcium iodate was prepared by addition of calcium chloride solution to potassium iodate, the precipitated salt being recrystallized and dried in vacuum over Anhydrone. The calcium paratoluene-sulphonate was prepared by neutralizing an aqueous solution of the acid almost to *p*H7 with calcium hydroxide; the salt was crystallized from the filtered mother liquor by boiling off water at 30°C under reduced pressure, recrystallized from water at 30°, and dried in vacuum over phosphorus pentoxide.

The results are given in Table I. In the first column, II indicates the autogenic cell with cadmium chloride as indicator, III *i* and III *p* the sheared cell with calcium iodate, and paratoluene sulphonate as indicator. The second column gives the concentration in equivalents per liter, the third the uncorrected value of t_+ or t_-, and the fourth the sum of the solvent and volume corrections.[4,8] The volume correction, $-C\Delta V/1000$, is given for cell II by

$$\Delta V=\tfrac{1}{2}\bar{V}_{CdCl_2}-\tfrac{1}{2}V_{Cd}-\tfrac{1}{2}t_+\bar{V}_{CaCl_2},$$

where V_{Cd} is the atomic volume of cadmium, t_+ is the transference number of calcium ion in chloride solution, and the other two symbols are the partial molal volumes of the salts in question. Since the cadmium anode forms the closed side of cell III, the volume correction in the sheared runs is the same as for cell II but with the opposite sign. The last column of the table gives the corrected value of $t_\pm$.

For purposes of comparison and interpolation, the deviation plot shown in Fig. 1 was used. Here the deviation δ is defined by

$$t_+=t_+^\circ-0.103\sqrt{C}+\delta, \qquad (1)$$

where t_+° is the transference number of calcium

TABLE II.

C	t_+, 15°	t_+, 25°	t_+, 35°
0.0	0.4334	0.4380	0.4427
0.005	0.4261	0.4307	0.4354
0.01	0.4231	0.4277	0.4424
0.02	0.4188	0.4234	0.4281
0.03	0.4156	0.4202	0.4249
0.05	0.4105	0.4151	0.4198
0.07	0.4067	0.4113	0.4160
0.10	0.4024	0.4070	0.4117
0.15	0.3964	0.4010	0.4057

[8] L. G. Longsworth, J. Am. Chem. Soc. **57**, 1185 (1935).

ion at infinite dilution; the values of $t_+°$, *viz.* 0.4334, 0.4380, and 0.4427 for 15°, 25°, and 35°, respectively, were obtained from the Λ_0 of the accompanying paper[9] and the revised values[10] of $\lambda_-°$ for chloride ion. It is apparent that within the precision of the measurements the change in transference number with concentration is independent of temperature—for this range at any rate; it will be remembered that the same was true for sodium chloride in aqueous solution between 15° and 45°C. It will also be noted that calcium chloride behaves normally in respect to the variation of the transference number with temperature for a given concentration, i.e., the transference numbers approach one-half as the temperature is increased. As Longsworth[8] has pointed out, however, the coefficient of the square root term in Eq. (1) is far from that predicted as a limiting law by the Debye-Onsager theory, e.g., −0.185 for 25°. Nevertheless, we believe that this method of plotting should give a reasonably accurate extrapolation to $0.005N$, a concentration low enough to interpret e.m.f. measurements on cells with transference. The smoothed values of t_+, given in Table II, correspond to the continuous curve of the figure.

The only previous measurements by the moving boundary method on calcium chloride solutions are those of Longsworth[8] at 25°C. His values of t_+ however, are uniformly about 0.001 less than those reported here. While the measurements on calcium chloride are not quite as reproducible as those for potassium and sodium chlorides, this discrepancy is nevertheless definitely greater than the apparent precision of either set of measurements. Thus Longsworth in his Table V gives for $0.02N$, $t_+=0.4226$ and $t_-=0.5776$, whose sum is unity within the precision of the measurements. From our Table I, the mean t_+ for $0.02N$ is 0.4234 and the mean t_- (from both iodate and paratoluene sulphonate boundaries) is 0.5768, the sum once again being unity within the same limits. Although Longsworth does not specifically say so, his measured transference numbers presumably were independent of the current, so that as far as internal evidence is concerned, it is difficult to make a decision as to the relative accuracy of the two sets of data. Even more puzzling is the fact that the conductances reported in the accompanying paper[9] are in satisfactory agreement with those of Shedlovsky and Brown,[5] and that the same is true of e.m.f. measurements on calcium chloride solutions carried out here and those of Shedlovsky and MacInnes;[11] this would seem to eliminate any serious divergence in technique in the preparation of the solutions in the two laboratories. It therefore seems evident that a final decision on this point can only come from a further independent investigation.

In conclusion we wish to express our thanks to Canadian Industries Limited for the grant to one of us (A.G.K.) of a fellowship.

[9] G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 470 (1945).

[10] G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 473 (1945).

[11] T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **59**, 503 (1937).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 11 NOVEMBER, 1945

The Conductance of Aqueous Solutions of Calcium Chloride at Temperatures from 15° to 45°C

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(Received August 2, 1945)

The conductance of aqueous solutions of calcium chloride at temperatures from 15° to 45°C has been determined by the direct-current method previously used for potassium chloride, sodium chloride, and potassium bromide. The results for 25° are in excellent agreement with those of Shedlovsky and Brown. At all temperatures the data can be represented by the extended Onsager-Shedlovsky equation, as in the case of the 1–1 salts. In contrast to the 1–1 salts, however, the contribution of the logarithmic term passes through a minimum with increasing temperature, and then rises. The limiting conductance has been determined for calcium ion; the temperature coefficient of the ionic conductance is large in comparison with those for univalent ions.

THIS research concerns the conductance of dilute aqueous solutions of calcium chloride at temperatures from 15° to 45°C; it is a natural complement to the work previously reported[1,2] from this laboratory on the conductance of the 1–1 salts potassium chloride, sodium chloride, and potassium bromide, and yields as well values of the limiting conductance and temperature coefficient for calcium ion when combined with the revised data for chloride ion reported in the accompanying paper.[3]

The measurements were carried out by the direct-current method previously described.[1] The only significant variation in technique lay in the determination of the solvent correction. Here, the correction was determined by adding to a weighed sample of the conductivity water to be used in making up the calcium chloride solution, a weighed amount of a $0.01N$ KCl solution so that the resulting concentration was approximately $5\times10^{-6}N$ in KCl, i.e., the conductance of the solution was caused in roughly equal amounts by the added salt and by the water. The specific conductance was then determined in a cell similar in all respects to that used in the calcium chloride measurements; by subtracting from the observed specific conductance, the known amount caused by the potassium chloride, the solvent correction was obtained at once. This method was found to give remarkably reproducible results, and had the advantage that both solution and solvent conductances were determined under as nearly identical conditions as possible.

The solutions were made by gravimetric dilution of stock solutions prepared as described in the preceding paper;[4] all weights have been reduced to vacuum, and in converting from mass to volume concentrations, the density data in *International Critical Tables*[5] have been used. Bath temperatures were set by means of a platinum resistance thermometer with National Bureau of Standards certificate, whose calibration has been checked repeatedly in this laboratory at the ice and Glauber's salt points.

Earlier measurements in this laboratory have been based on Jones and Prendergast's 0.01 Normal standard;[6] the reasons for selecting this rather than the more generally used Jones and Bradshaw[7] 0.01 Demal standard have been discussed in reference 1. We have been informed by

TABLE I.

10^4C	97.232	99.136	99.421	99.454	98.929
Λ	120.55	120.42	120.43	120.41	120.45
Λ_0'	138.17_3	138.22_1	138.26_0	138.24_3	138.23_3
$\Lambda_0'\ _{C=0.01}$	138.25_7	138.24_7	138.27_8	138.26_0	138.26_5

* Canadian Industries Limited Fellow in Chemistry, 1944–1945.

[1] H. E. Gunning and A. R. Gordon, J. Chem. Phys. **10**, 126 (1942).

[2] H. E. Gunning and A. R. Gordon, J. Chem. Phys. **11**, 18 (1943).

[3] G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 473 (1945).

[4] A. G. Keenan, H. G. McLeod, and A. R. Gordon, J. Chem. Phys. **13**, 466 (1945).

[5] *International Critical Tables*, Vol. 3, p. 72.

[6] Grinnell Jones and M. J. Prendergast, J. Am. Chem. Soc. **59**, 731 (1937).

[7] Grinnell Jones and B. C. Bradshaw, J. Am. Chem. Soc. **55**, 1780 (1933).

Dr. B. B. Owen,[8] however, that while Jones and Prendergast's hundredth Normal and tenth Normal standards are slightly more self-consistent than are the Demal when tested by Shedlovsky, Brown, and MacInnes' Eq. (7), the actual experimental results[9] of Shedlovsky, Brown, and MacInnes indicate no significant superiority of the Normal standards over the Demal; we have therefore used the Jones and Bradshaw $0.01D$ standard at 25° for purposes of calibration.

Owing to the large number of measurements, we have recorded in Table III not the results of individual runs but averages for a number of experiments carried out at approximately round values of the concentration. The method by which these averages were obtained (and incidently an idea of the self-consistency of the data) may be illustrated by taking the entry for $0.01N$ solution at 25° as an example. The first line of Table I gives the actual concentrations in equivalents per liter for a number of measurements near this concentration; the solution in each is the result of a dilution from a different stock solution. The second line of the table gives the observed equivalent conductance, corrected for solvent conductance, and the third line the corresponding Λ_0' (see Eq. (1) below). From a large scale plot of all the data for this temperature, a value of $d\Lambda_0'/dC$ at $C=0.01$ was determined; for the narrow range of concentration involved, this could be taken as constant for the table. From the difference in concentration from $0.01N$, and the known value of $d\Lambda_0'/dC$ *viz.*, 304, it was then possible to calculate the Λ_0' for $C=0.01$ corresponding to each of the observed values of Λ_0' in the third line. The results are entered in the fourth line of the table, the mean of the entries being $138.26_2 \pm 0.00_8$; this corresponds to $\Lambda = 120.38 \pm 0.01$, which is the value entered in Table III.

TABLE II.

	15°	25°	35°	45°
Λ_0	108.40	135.85	165.48	197.11
t_-°	0.5666	0.5620	0.5573	0.5525
ϑ	0.4844	0.4942	0.5052	0.5177
3σ	85.87	110.49	138.08	167.93
B	472	529	615	894
D	147	144	155	270

TABLE III.

10^4C	15°C Λ_{obs}	Λ_{calc}	10^4C	25°C Λ_{obs}	Λ_{calc}
5	105.30	105.30	5	131.90	131.90
10	104.05	104.04	10	130.32	130.33
20	102.35	102.36	20	128.20	128.18
30	101.11	101.12	30	126.61	126.60
50	99.28	99.26	50	124.23	124.24
70	97.89	97.86	70	122.47	122.45
100	96.24	96.25	100	120.38	120.38
	35°C			45°C	
5	160.58	160.57	5	191.09	191.07
10	158.64	158.62	10	188.65	188.66
20	155.97	155.95	20	185.34	185.36
30	153.98	153.99	30	182.94	182.94
50	151.03	151.05	50	179.34	179.33
70	148.84	148.82	70	176.65	176.61
100	146.21	146.21	100	173.43	173.47

The results are summarized in Table III as a function of the concentration in equivalents per liter. As Shedlovsky and Brown[10] have shown, a suitable analytic representation may be obtained by the use of the Onsager-Shedlovsky equation, just as in the case of the 1–1 salts:[9, 11]

$$(\Lambda+3\sigma\sqrt{C})/(1-\vartheta\sqrt{C}) = \Lambda_0' = \Lambda_0 + BC + DC\log C, \quad (1)$$

where for a 2–1 electrolyte ϑ and σ are given by[12]

$$\vartheta = (4.5734\times10^6/(DT)^{\frac{3}{2}})/(1+t_-^\circ+0.8165(1+t_-^\circ)^{\frac{1}{2}}), \quad (2)$$

$$\sigma = 50.435/\eta(DT)^{\frac{1}{2}}, \quad (3)$$

where D is the dielectric constant, η the viscosity of water, and t_-° is the transference number of the chloride ion at infinite dilution. Since t_-° can only be computed from λ_-° for chloride ion if Λ_0 is known, the extrapolation to infinite dilution by means of Eq. (1) requires a short series of approximations. The final values of Λ_0, and the corresponding t_-° (obtained from these and the revised values of λ_-° listed in Table III of the accompanying paper[3]) are summarized in Table II.

[8] B. B. Owen, private communication.
[9] T. Shedlovsky, A. S. Brown, and D. A. MacInnes, Trans. Am. Electrochem. Soc. 66, 165 (1934).
[10] T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. 56, 1066 (1934).
[11] A. R. Gordon, J. Chem. Phys. 7, 221 (1939).
[12] The values of the universal constants used to compute the coefficients ϑ and σ are those recommended by Manov, Bates, Hamer, and Acree (J. Am. Chem. Soc. 65, 1765 (1943)). The dielectric constants are those of Wyman (Phys. Rev. 35, 623 (1930)) and the viscosities are from *International Critical Tables*, Vol. 6, p. 234.

TABLE IV.

	15°	25°	35°	45°
$(\lambda_+^\circ)_{\frac{1}{2}Ca^{++}}$	46.98	59.50	73.26	88.21
$d \ln \lambda_+^\circ/dT$	0.0252_5	0.0221_0	0.0196_0	0.0176_5

The table also gives the values of ϑ and σ and of the coefficients B and D of Eq. (1); the latter are, of course, entirely empirical, and are chosen to give the best fit with the data. That Eq. (1) does give an excellent representation is evident from the columns headed Λ_{calc} in Table III, the differences between "observed" and "calculated" being in general no greater than the precision of the measurements.

Although the physical interpretation of the coefficients[13] B and D of Eq. (1) is a matter of uncertainty, a comparison of the results obtained here with those for the 1–1 salts (see Table I of reference 3) is nevertheless of interest. In the first place, the values for calcium chloride are much greater, i.e., the deviation of the conductance from the limiting Onsager equation is greater than for potassium chloride, potassium bromide, and sodium chloride. Secondly, B and D for calcium chloride, though large, are not such as to cause Λ_0' to pass through a minimum[14] at any concentration investigated; in other words, a plot of the data of Table III against the square root of the concentration would lie everywhere above the Onsager limiting slope. Conductances which lie below the limiting slope at moderately low concentrations, as in the case of potassium and silver nitrate in aqueous solution,[15] have been interpreted as evidence for ion association in solution; on this basis, calcium chloride is as "strong" an electrolyte as potassium and sodium chlorides. Finally it should be noted that the contribution of the logarithmic term for a given concentration passes through a minimum with increasing temperature; this is in contrast to the behavior of the 1–1 salts, for which its importance, both absolutely and relatively, decreases rapidly with rising temperature.

The most extensive precise measurements on the conductance of calcium chloride solutions in the literature are those of Shedlovsky and Brown[10] at 25°C. A comparison of the smoothed entries in their Table VI with the 25° data in our Table III shows that the agreement between the two sets of measurements is most satisfactory; in only one instance is the discrepancy as great as 0.03 conductance unit.

The values of the limiting ionic conductance for calcium ion are given in Table IV; they were obtained from the Λ_0 of Table II and the known values of λ_-° for chloride ion (see Table III of reference 3). The table also lists the temperature coefficient of the conductance for calcium ion; the values were obtained by differentiation of a cubic equation fitted to $\ln \lambda_+^\circ$ for the four temperatures. A comparison of these values with those for the univalent ions[3] shows that calcium ion has a larger temperature coefficient than sodium ion although it is from 15 percent to 20 percent faster. Such temperature coefficients have been interpreted[16–18] as a measure of the energetics of the transport process; it is evident, however, that the statement that large slow ions must naturally have larger activational energies of transport and consequently larger temperature coefficients than small fast ions is an oversimplification. The evidence obtained here and in the earlier papers[1,2] indicates that the Kohlrausch rule can only be true if the ions to be compared are of the same charge and sign, and this is, after all, not surprising.

In conclusion, we wish to express our thanks to Canadian Industries Limited for the grant to one of us (G. C. B.) of a fellowship, and to Mr. Harold Schiff of this Department for his assistance in making some of these measurements.

[13] L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932).

[14] It should be noted that the use of Eq. (1) necessitates a minimum for Λ_0' at a concentration given by $\ln C = -(2.303B+D)/D$. For calcium chloride at 15°, this concentration is $0.00023N$, at which Λ_0' is 0.015 conductance unit less than Λ_0; for higher temperatures, this concentration is still lower. Similarly, with potassium and sodium chlorides at 15°, the minimum Λ_0' occurs at approximately $0.0005N$, and is less than the corresponding Λ_0 by 0.01_5 unit in both cases.

[15] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932). The minima for the two nitrates occur, however, at concentrations much higher than those discussed in footnote 13—approximately $0.0025N$; moreover, the minimum Λ_0' for the potassium and silver salts are approximately one-quarter and one-tenth of a conductance unit less than the corresponding Λ_0; see reference 11.

[16] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

[17] H. S. Taylor, J. Chem. Phys. **6**, 331 (1938).

[18] M. J. Polissar, J. Chem. Phys. **6**, 833 (1938).

A Reinvestigation of the Conductance of Aqueous Solutions of Potassium Chloride, Sodium Chloride, and Potassium Bromide at Temperatures from 15° to 45°C

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(Received August 2, 1945)

The conductance of aqueous solutions of potassium chloride, sodium chloride, and potassium bromide has been redetermined by the direct-current method at temperatures from 15° to 45°C. It is found that on the whole the present measurements satisfactorily confirm the earlier work reported from this laboratory; however, there were apparently slight errors in the temperature scale at 35° and 45° corresponding to a few hundredth's of a percent in the conductance. Revised values of the conductance, of the limiting ionic conductance and its temperature coefficient, and of the coefficients in the Onsager-Shedlovsky equation are tabulated.

IN the course of the work reported in the preceding paper[1] we have reinvestigated the conductance of potassium chloride, sodium chloride, and potassium bromide in aqueous solution at temperatures from 15° to 45°C by the direct-current method. The apparatus and technique were the same as were previously employed.[1–3] Bath temperatures were fixed directly with the platinum resistance thermometer which is temperature standard for this laboratory; its calibration by the U. S. National Bureau of Standards has been checked repeatedly at the ice and Glauber Salt points. As in the case of calcium chloride,[1] the measurements are based on the Jones and Bradshaw[4] 0.01 Demal standard at 25° rather than on the Jones and Prendergast[5] 0.01 Normal standard previously employed; this has the effect of decreasing all the conductances 0.021 percent as compared with those previously reported.

We find that the earlier measurements for 35° and 45° correspond in general to temperatures slightly more than 0.01° too high; the exceptions are the sodium chloride data[2] for 35° (for which the previous temperature was approximately 0.02° too high) and the potassium bromide results[3] at 45° where the previous temperature was approximately 0.01° too low. To save space, Table I gives the values of the constants in the Onsager-Shedlovsky equation

$$(\Lambda+2\sigma\sqrt{C})/(1-\vartheta\sqrt{C}) = \Lambda_0+BC+DC\log C, \quad (1)$$

TABLE I.

	15°	25°	35°	45°
ϑ	0.2249	0.2289	0.2335	0.2387
2σ	46.76	60.18	75.20	91.44
Λ_0, KCl	121.07	149.85	180.42	212.41
B, KCl	217	154	150	158
D, KCl	76	32	16	6
Λ_0, NaCl	101.18	126.45	153.75	182.65
B, NaCl	210	107	137	159
D, NaCl	73	3	2	0
Λ_0, KBr	122.81	151.64	182.24	214.17
B, KBr	105	108	143	165
D, KBr	6	0	0	0

TABLE II.

10^4C	0	5	10	20	50	100
			Λ for potassium chloride			
15°	121.07	119.40	118.72	117.78	116.04	114.31
25°	149.85	147.76	146.92	145.76	143.56	141.27
35°	180.42	177.85	176.81	175.38	172.68	169.84
45°	212.41	209.30	208.05	206.33	203.07	199.62
			Λ for sodium chloride			
15°	101.18	99.61	98.98	98.10	96.47	94.86
25°	126.45	124.51	123.74	122.66	120.64	118.53
35°	153.75	151.33	150.38	149.04	146.55	143.94
45°	182.65	179.71	178.54	176.93	173.88	170.70
			Λ for potassium bromide			
15°	122.81	121.19	120.54	119.66	118.00	116.28
25°	151.64	149.57	148.75	147.61	145.46	143.20
35°	182.24	179.68	178.66	177.26	174.62	171.86
45°	214.17	211.06	209.83	208.12	204.90	201.52

* Canadian Industries Limited Fellow in Chemistry, 1944–1945.

[1] G. C. Benson and A. R. Gordon, J. Chem. Phys. **13**, 470 (1945).

[2] H. E. Gunning and A. R. Gordon, J. Chem. Phys. **10**, 126 (1942).

[3] H. E. Gunning and A. R. Gordon, J. Chem. Phys. **11**, 18 (1943).

[4] Grinnell Jones and B. C. Bradshaw, J. Am. Chem. Soc. **55**, 1780 (1933).

[5] Grinnell Jones and M. J. Prendergast, J. Am. Chem. Soc. **59**, 731 (1937).

TABLE III.

	15°	25°	35°	45°
($\lambda_-°$) Cl_-, KCl	61.41	76.35	92.21	108.92
($\lambda_-°$) Cl_-, NaCl	61.43	76.35	92.22	108.88
($\lambda_-°$) Br_-, KBr	63.15	78.14	94.03	110.68
($\lambda_+°$) K_+, KCl	59.66	73.50	88.21	103.49
($\lambda_+°$) Na_+, NaCl	39.75	50.10	61.53	73.77
($\lambda_+°$) H_+, HCl	300.6	349.82	397.0	441.4

TABLE IV.

	$d \ln \lambda_\pm°/dT$			
	15°	25°	35°	45°
Cl_-	0.02340	0.02020	0.01765	0.01570
Br_-	0.02285	0.01980	0.01730	0.01535
K_+	0.02235	0.01950	0.01705	0.01500
Na_+	0.02445	0.02180	0.01930	0.01695
H_+	0.01655	0.01385	0.01155	0.00970

which represent the revised data within experimental precision; the values of the theoretical coefficients ϑ and σ are those previously employed.[1,2] Table II gives the conductance, computed by Eq. (1), for a few round values of the concentration C in moles per liter. When the altered calibration and (at 35° and 45°) the correction for temperature are born in mind, it will be noted that as far as dependence of conductance on concentration is concerned, these results are practically indistinguishable from those previously reported.

Table III gives the revised values of the ionic conductances at infinite dilution. The entries for chloride, potassium, and sodium ions were obtained from the Λ_0 of Table I and the limiting transference numbers.[6,7] It will be noted that the agreement between $\lambda_-°$ for potassium chloride and sodium chloride at 35° is closer than was previously reported, but that for 45° it is slightly worse; at all temperatures, however, it is within the precision of the transference measurements. The $\lambda_-°$ for bromide ion were obtained by difference from the Λ_0 for KBr and the $\lambda_+°$ for K_+. The table also includes for comparison $\lambda_+°$ for hydrogen ion, obtained from the conductance measurements of Shedlovsky[8] and of Owen and Sweeton[9] and the values of $\lambda_-°$ for chloride ion; these differ from those of Owen and Sweeton by 0.3-conductance units at 15° and 35° and by 0.6-conductance units at 45°; the discrepancy is caused by the transference numbers Owen and Sweeton employed. Table IV gives the temperature coefficients for the limiting ionic conductance; these were obtained by differentating cubic equations fitted to the values of $\ln \lambda°$ for the four temperatures.

When allowance is made for the change in calibration, the revised data in Tables II, III, and IV differ in general from those previously reported by but little more than the precision[10] of the measurements; our present values nevertheless are, we believe, the more reliable, and are moreover self-consistent in the temperature.

[6] R. W. Allgood, D. J. Le Roy, and A. R. Gordon, J. Chem. Phys. **8**, 418 (1940).

[7] R. W. Allgood and A. R. Gordon, J. Chem. Phys. **10**, 124 (1942).

[8] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).

[9] B. B. Owen and F. H. Sweeton, J. Am. Chem. Soc. **63**, 2811 (1941).

[10] For a discussion of the correlation of the results obtained by the direct-current method with those given by the more usual alternating-current bridge, see references 1, 2, and 3.

Effect of Pressure on the Melting of Crystalline Rubber

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The temperature of melting of a sample of stark rubber has been found to increase from about 36° to 70°C as the pressure is raised from 1 to 1170 bars.

THE effect of hydrostatic pressure on the melting of crystalline rubber has been the subject of a brief investigation extending to pressures above 1000 atmospheres. With a particular sample of stark rubber it was found possible to raise the temperature of melting, as determined by the disappearance of birefringence, from about 36° to 70°C by the application of a pressure of 1170 bars (1170×10^6 dynes/cm²). The results, including observations at intermediate pressures, are given in Table I and in Fig. 1.

The crystalline smoked-sheet sample, called stark rubber since it had a melting range above room temperature, was furnished in 1939 by Dr. H. I. Cramer while he was a professor at the University of Akron.

Melting of a portion of this sample at atmospheric pressure was determined from observations of volume changes in a mercury-filled dilatometer by a method previously described.[1,2] It can be seen from Fig. 2 that the melting occurred over a range of temperature from 32° to 39°C. The disappearance of the birefringence, which according to Fig. 1 takes place close to 36°C at atmospheric pressure, evidently defines a position near the center of the melting range.

The expansivity, $(1/V)(dV/dT)$, at 25°C of the amorphous rubber calculated from data plotted in Fig. 2 is found to be 650×10^{-6} per degree C and that of the crystalline rubber 590×10^{-6} per degree C.

The high pressure equipment used in this investigation was located in the Geophysical Laboratory of the Carnegie Institution of Washington

TABLE I. Pressure and related quantities at temperature of melting.

Temperature of melting	Pressure Obs.	Pressure Calc.	dT/dp Calc.	$L/\Delta V$ Calc.
°C	bars	bars	deg./bar	joules/cm³
36.2	—	1	0.0365	846
40	106	108	.0345	906
45	259	258	.0323	987
50	433	419	.0302	1060
55	586	590	.0283	1160
65	967	966	.0250	1350
70	1170	1172	.0236	1450

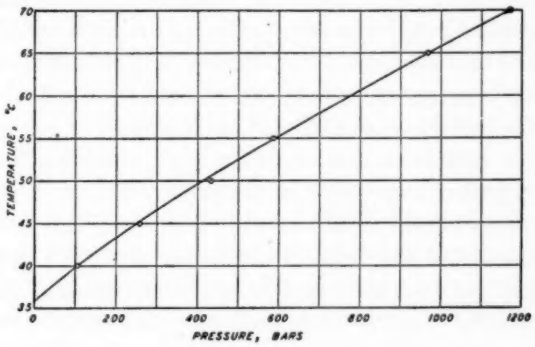

FIG. 1. Relation between temperature of melting and applied pressure for a sample of stark rubber.

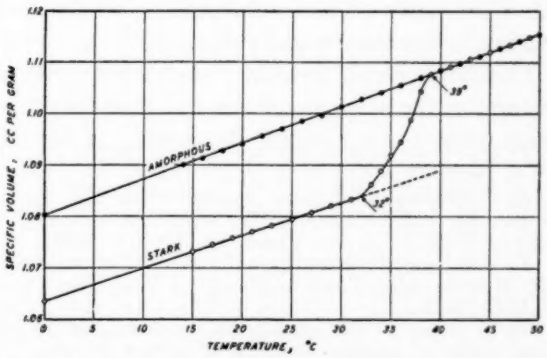

FIG. 2. Relation between specific volume and temperature at atmospheric pressure for the sample of stark rubber, before and after melting.

[1] N. Bekkedahl, "Forms of rubber as indicated by temperature-volume relationship," J. Research Nat. Bur. Stand. **13**, 411 (1934); Research Paper RP717. Reprinted in Rubber Chem. Tech. **8**, 5 (1935).

[2] N. Bekkedahl and L. A. Wood, "Crystallization of vulcanized rubber," Ind. Eng. Chem. **33**, 381 (1941). Reprinted in Rubber Chem. Tech. **14**, 347 (1941).

and has been described in previous papers.[3,4] The approximate adjustment of the pressure was made by means of a hand-pump and the fine adjustment by a screw-plunger operated by a wheel. The amount of pressure was determined by a calibrated manganin wire resistance-gage.[5,6]

Specimens of the stark rubber sample were cut into strips about a millimeter in thickness. One strip of this stark rubber, together with a similar strip previously melted by heating to about 70°C, were placed side by side in a glass piezometer. The use of two specimens adjacent to each other permitted an excellent visual criterion for determining when birefringence disappeared.

Ethylene glycol was used as a confining liquid in the piezometer. Water was found to be unsatisfactory for this purpose since it penetrated the rubber specimens and impaired their transparency after several hours at high pressures. No such difficulty was encountered with the ethylene glycol.

Light from a 6-volt, 32-candle-power lamp, after being polarized by a sheet of Polaroid, passed through the window of the pressure equipment and through the specimen. It was observed, after emerging from the equipment, by the use of a second sheet of Polaroid as analyzer.

In operation, the piezometer containing the specimens was placed in the apparatus, the pressure increased to about 1300 bars, and the temperature of the bath raised to the desired value. After temperature equilibrium was attained, the pressure was slowly lowered and continuous observations made of the birefringence. Except during the melting of the stark specimen, no significant variation with pressure was noted in the appearance of the birefringence of the two specimens between crossed Polaroids.

The change in birefringence associated with the melting of the stark specimen was found to take place over a small range of pressure, with the major portion of the change occurring within an interval of only a few bars. The pressure at which the change of birefringence was most rapid has been used as abscissa in Fig. 1, and the corresponding bath temperature used as ordinate. A new specimen, cut from the same sheet of stark rubber, was required for each point. The data from which the curve was plotted are given in the first two columns of Table I.

The relation between the temperature of melting and the pressure shown by the curve cannot be regarded as valid for crystalline rubber having at atmospheric pressure a melting range different from that described here. Since the melting range at atmospheric pressure is dependent on the temperature at which the crystals were formed,[7] this fact limits the application of the present results. However, if a study were to be made of rubber crystallized at different temperatures, it is presumed that as a first approximation a family of curves not too far from parallel would be obtained, with displacement along the temperature axis.

Some crystallization was observed when amorphous specimens were kept under a pressure of about 1100 bars at 30°C for 16 hours. It was observed that the crystals formed in this manner melted at a much lower temperature than the value for the same pressure given by the curve in Fig. 1. The crystals formed under these conditions were evidently different from those present originally in the stark rubber. At atmospheric pressure the temperature of melting, as already mentioned, is dependent on the temperature at which the crystals were formed. No doubt the melting depends in a somewhat similar fashion on the pressure on the rubber during crystallization.

At atmospheric pressure rubber crystallizes at temperatures between −50°C and +15°C, crystallizing most rapidly at temperatures near −25°C. The effect of an increase of pressure is to raise the range of temperatures at which crystallization may occur. For example, Thiessen and Kirsch[8–10] found that pressures up to 25 atmos-

[3] R. E. Gibson and John F. Kincaid, "The influence of temperature and pressure on the volume and refractive index of benzene," J. Am. Chem. Soc. **60**, 511 (1938).

[4] R. E. Gibson, "The compressions of solutions of certain salts in water, glycol, and methanol," J. Am. Chem. Soc. **59**, 1521 (1937).

[5] R. E. Gibson, "The influence of concentration on the compressions of aqueous solutions of certain sulfates," J. Am. Chem. Soc. **56**, 4 (1934).

[6] R. E. Gibson, "The influence of the concentration and nature of the solute on the compressions of certain aqueous solutions," J. Am. Chem. Soc. **57**, 284 (1935).

[7] N. Bekkedahl and L. A. Wood, "Influence of the temperature of crystallization on the melting of crystalline rubber," J. Chem. Phys. **9**, 193 (1941). Reprinted in Rubber Chem. Tech. **14**, 544 (1941).

[8] P. A. Thiessen and W. Kirsch, "Crystallization of rubber by pressure," Naturwiss. **26**, 387 (1938). Translated in Rubber Chem. Tech. **12**, 12 (1939).

[9] P. A. Thiessen and W. Kirsch, "Crystallization of

pheres increased the rate of crystallization at temperatures near 10°C. Dow[11] observed that a pressure of 8000 kg/cm² raised the range of temperature favorable for crystallization so much that no crystals were formed during 14 days at 0°C. The partial crystallization after 16 hours at 30°C under a pressure of 1100 bars in the present work is additional evidence of the same effect.

The curve shown in Fig. 1 can be represented adequately by the 3-constant logarithmic equation,

$$\log_{10}(p+1300)=5.9428-875/T,$$

where T is the temperature of melting in degrees Kelvin and p is the pressure in bars. The values given in the third column of Table I are calculated from the above equation. A differentiation of the equation gives

$$dT/dp=T^2/2015(p+1300),$$

from which the values in the fourth column of the table were calculated.

The use of the Clapeyron equation,

$$dp/dT=L/T\Delta V$$

where L is the heat of fusion and ΔV the corresponding change in volume, permits a calculation of $L/\Delta V$ from the data just given. This quantity, in joules per cubic centimeter of volume change, is shown in the last column of the table.

From the dilatometric measurements represented by the graph in Fig. 2, ΔV was found to be 0.0191 cm³ per gram of rubber at 36.2°C. From these data the value of L for this sample is calculated to be 16.2 joules per gram.

Other observations in this laboratory have shown that this sample of stark rubber could undergo additional crystallization at lower temperatures. The full heat of fusion should include the contribution of these additional crystals which were observed to form at the lower temperatures. Therefore we do not regard the value just given as the full heat of fusion of crystalline rubber at 36.2°C. A direct measurement[12] of the heat of fusion of another sample of rubber melting over a range centered at about 11°C yielded 16.7 joules per gram. The corresponding value at 36.2°C might be expected to be larger than that at 11°C. The terms ΔV and T in the Clapeyron equation are both larger at the higher temperature, but a lack of data regarding the values of dp/dT at 1 bar for samples melting between 11° and 36.2°C prevents drawing a definite conclusion. In spite of the impossibility of making an exact calculation with the data available the agreement in order of magnitude is quite satisfactory.

The rate of change of melting temperature with pressure is observed to have the value 0.037°C per bar at the lowest pressures and to decrease with increasing pressure to a value of about 0.024°C per bar at 1170 bars. The average value over the range studied is 0.029°C per bar. This is considerably lower than the average value calculated from a single observation of Dow[11] who found rubber crystallized at 0°C to melt at 77.5°C under a pressure of 1270 kg/cm². From this observation one may calculate a value of 0.052°C per bar if 11°C is taken as the melting temperature at atmospheric pressure for rubber crystallized at 0°C.[1]

The experimental observations for the present investigation were made in the summer of 1940, but earlier publication was prevented by war activities, which also led to the abandonment of a more extensive investigation which had been planned.

weakly vulcanized rubber by pressure," Naturwiss. **27**, 390 (1939). Translated in Rubber Chem. Tech. **13**, 48 (1940).

[10] W. Kirsch, *Equilibria between Crystals and Melts in Rubber and Their Dependency on Temperature and Pressure*, Dissertation (Trillsch and Huther, Berlin, 1937).

[11] R. B. Dow, "Inhibition of crystallization of rubber by high pressure," J. Chem. Phys. **7**, 201 (1939). Reprinted in Rubber Chem. Tech. **12**, 496 (1939).

[12] N. Bekkedahl and H. Matheson, "Heat capacity, entropy, and free energy of rubber hydrocarbon," J. Research Nat. Bur. Stand. **15**, 503 (1935); Research Paper RP844. Reprinted in Rubber Chem. Tech. **9**, 264 (1936).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 11 NOVEMBER, 1945

Free Volume and Entropy in Condensed Systems

I. General Principles. Fluctuation Entropy and Free Volume in Some Monatomic Crystals

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In a system of atoms whose motions are classically excited, the change in entropy in any isothermal process can be written $R \ln (V_{f2}/V_{f1})$ per mole, one such term for each kind of atom in the system. The free volume V_f used in this expression is the effective volume accessible to the centers of gravity of the atoms, corrected for fluctuation effects. Corresponding expressions can be written for the classical (translational or rotational) part of the motions of polyatomic molecules in real liquids and solids. In solids the free volume can be written $V_f = Nvf$, where v is a box, or cage, volume accessible to one particle, and f, the fluctuation factor, has a numerical value which depends on the way in which the box is defined. $R \ln f$ is a contribution to the entropy of the system, and the name "fluctuation entropy" is proposed for it. The fluctuation entropy includes what has been called "communal entropy" as well as a term due to the temperature variability of cell sizes. The free volume in a monatomic crystal can be determined from thermodynamic data, one convenient relationship being $P_{vap} = (RT/V_f) \exp(-\Delta H/RT)$. When this is applied to the data for the vapor pressures of the solids A, Kr, Xe, Mg, Zn, Cd, Hg, values of V_f are obtained which are about ½ percent of the volumes of the solids. The values of f found for these crystals support Rice's view that solids should display a rather large fluctuation entropy.

INTRODUCTION

ONE of the outstanding features of the scientific history of the past twenty years has been the growing up, so to speak, of statistical mechanics.[1] This was made possible by the development of the quantum mechanics, and, in its turn, provided methods and points of view from which it became possible to discuss many old problems with new precision. One of the developments which have ensued is the concerted attack which has been made, within the last seven or eight years, on the problems of the liquid state. Discussions of this attack, the different directions from which it is being made, and the kind of success which it has attained, have been given in several recent treatments,[2] in which extended bibliographies may be found. The current situation is that a rather good qualitative understanding of liquids is now at our disposal. Moreover, many special models have been proposed, which have made possible successful quantitative treatments of the cases for which they have been developed. There still does not exist, however, a picture which is at once general enough and precise enough to permit the discussion, within a single framework, of all of the data on liquids, and on solutions, which need explanation, and which should in principle be able to serve as ammunition in the attack.

In the attempt to obtain such a picture it seems that the idea of free volume[3] should play an important part, if properly developed and used. This is because it is, on the one hand, a pictorial idea, and, on the other, is capable of being brought into an exact relationship with thermodynamics.

The present paper and the two which follow constitute an essay in the elaboration and application of the free volume concept. It turns out that the application makes possible, among other things, the pictorial interpretation of certain entropy rules obtained empirically by Barclay and Butler,[4] Bell,[5] and others[6] as well as of certain

[1] Compare, for example the books by J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940) and R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1940) with that of R. C. Tolman, *Statistical Mechanics* (Chemical Catalog Company, New York, 1927).

[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Chapter 14, particularly Section *l*; R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Chapter VIII; G. Jaffe, Phys. Rev. **62**, 463 (1942); O. K. Rice, J. Chem. Phys. **12**, 1 (1944).

[3] See note 2, and papers by Eyring and his collaborators, e.g., H. Eyring and J. O. Hirschfelder, J. Phys. Chem. **41**, 249 (1937); J. F. Kincaid and H. Eyring, J. Chem. Phys. **6**, 620 (1938).

[4] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).

[5] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

[6] E.g., M. G. Evans and M. Polanyi, Trans. Faraday Soc. **32**, 1333 (1936).

departures of solutions from "regularity" in the Hildebrand[7] sense. The point of view which is developed also makes it possible to discuss the anomalies of aqueous solutions of non-polar substances, and finally, to draw some new conclusions from the numerical values of the entropies of hydration of ions. These should be of importance for future developments in electrolyte theory.

GENERAL CONSIDERATIONS

The way in which free volume has been introduced in previous work, and the precise implications of the definitions which have been offered, have differed from author to author, and sometimes, for the same author, from time to time.[8] Some of the definitions have been fundamentally equivalent to the one employed in this paper, but so far as the writer is aware, no previous discussion follows quite the same method of development as is used here. This consists first in establishing a correlation of very general validity between the free volume as defined by ΔS for an isothermal process, and one obtained from a physical picture. From a study of simple systems rules are obtained by which the "picture" free volume can always be made to equal the "thermodynamic" free volume. It is then possible to use experimentally determined entropy changes to draw rather detailed conclusions about the physical nature of the systems concerned. Of course, physical pictures are things which we make for ourselves, and their use is optional, not obligatory. This means, among other things, that free volume is an auxiliary concept, with only such meaning as is put into it by the definition adopted. It follows that any correct statement that can be made with it, or about it, must correspond to an equally good statement which does not involve free volume at all. This does not mean, however, that the concept is without value. On the contrary it can be used, and is used in these papers, to derive, and make pictorial, entropy relations which are otherwise difficult to arrive at or to understand.

DIATOMIC ASSOCIATIONS

As an introduction to some necessary ideas, we begin the discussion of the relation between free volume and entropy by considering a case for which explicit and rigorous expressions can be written for all the quantities of interest, namely the association of two atoms to form a diatomic molecule. Specifically, consider the entropy change per mole when two ideal monatomic gases X and Y unite at constant volume to form the ideal diatomic gas XY. For any ideal gas the entropy per mole is

$$S=R[\ln (Q/N)+T(d \ln Q/dT)+1]$$

where Q is the partition function, and N is Avogadro's number. Therefore

$$\Delta S=S_{XY}-S_X-S_Y$$

$$=R\left[\ln\left(\frac{NQ_{XY}}{Q_XQ_Y}\right)+T\frac{d}{dT}\left(\ln\frac{Q_{XY}}{Q_XQ_Y}\right)-1\right] \quad (1)$$

$$Q_X=Q_{iX}\frac{(2\pi m_XkT)^{\frac{3}{2}}}{h^3}V,$$

where Q_{iX} is the partition function of X corresponding to nuclear and electronic energies, m_X is the mass of an X atom, V is the volume of the reaction vessel, and the other symbols have their usual meaning. Correspondingly,

$$Q_Y=Q_{iY}\frac{(2\pi m_YkT)^{\frac{3}{2}}}{h^3}V.$$

We now make some assumptions, the importance of which will be discussed later. We assume that the temperature is high enough to justify using classical partition functions for the rotational and vibrational motions of XY. We also assume that the vibration of XY is simply harmonic, i.e., obeys the law

$$r-r_0=A \sin (2\pi\nu t+\varphi), \quad (2)$$

and that the amplitude A is very small compared with the equilibrium separation r_0. Here $\nu=(1/2\pi)(f/\mu)^{\frac{1}{2}}$, where f is the effective restoring force constant, and μ is the reduced mass, equal to

[7] J. H. Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929); or *Solubility* (Reinhold Publishing Corporation, New York, 1936), p. 65.

[8] E.g., O. K. Rice, J. Chem. Phys. **5**, 353 (1937), where an "internal volume" is defined in terms of an entropy change; Eyring (see references in note 3) writes a partition function for a liquid where E is sometimes temperature-dependent and sometimes not.

$(m_X m_Y)/(m_X+m_Y)\cdot\varphi$ is an unknown phase constant. Since X and Y are assumed not to be identical, the symmetry number of the XY molecule is 1 and

$$Q_{XY}=Q_{iXY}\frac{[2\pi(m_X+m_Y)kT]^{\frac{3}{2}}}{h^3}V\cdot\frac{8\pi^2IkT}{h^2}\cdot\frac{kT}{h\nu}. \quad (3)$$

Substituting for ν, and remembering that I, the moment of inertia, equals μr_0^2, we can rewrite (3)

$$Q_{XY}=Q_{iXY}\frac{[2\pi(m_X+m_Y)kT]^{\frac{3}{2}}}{h^3}\cdot\frac{[2\pi\mu kT]^{\frac{3}{2}}}{h^3}\cdot V\cdot 4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}. \quad (4)$$

Since $(m_X+m_Y)\mu=m_X m_Y$ we can obtain from (4)

$$\frac{Q_{XY}}{Q_X Q_Y}=\frac{Q_{iXY}}{Q_{iX}Q_{iY}}\cdot\frac{4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}}{V}. \quad (5)$$

The contribution of nuclear multiplicities to the quotient of Q_i's will be a factor of unity by a general theorem.[9] The contribution on account of electronic multiplicities will in general not be unity. We may call it F_e. It will be independent of temperature if the lowest energy for electronic excitation both of the molecule XY and of the atoms X and Y is large compared to kT, and we shall assume this to be the case. Then with (5) and (1)

$$\Delta S=R\left[\ln F_e+\ln\left\{\frac{N\cdot 4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}}{V}\right\}+\tfrac{1}{2}-1\right]. \quad (6)$$

We may assume, as usual, that on the average an XY molecule spends only a very small fraction of its time in collision with other molecules or atoms. Between collisions it will be vibrating according to the law (2) with an amplitude A. The energy of this vibrational state is given by $\epsilon=\frac{1}{2}fA^2$. The average value of A over an assembly in thermal equilibrium is given by

$$\bar{A}=\left(\int Ae^{-\epsilon/kT}dpdq\right)\Big/\left(\int e^{-\epsilon/kT}dpdq\right),$$

which may be evaluated without difficulty to give $\bar{A}=(\pi kT/2f)^{\frac{1}{2}}$. Since we have assumed $A\ll r_0$, and $r-r_0$ varies between $-A$ and $+A$ in any vibration,

$$4\pi r_0^2\cdot 2\bar{A}=4\pi r_0^2\cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}$$

is the average volume of the spherical shell about an X atom within which the Y atom partner is to be found, or *vice versa*. If we call this v, (6) becomes

$$\Delta S=R\left[\ln F_e+\ln\frac{Nv}{V}-\tfrac{1}{2}\right]. \quad (7)$$

Apart from the terms $R\ln F_e$ and $-\frac{1}{2}R$, we see that in the association reaction the entropy change is the same as would have been produced by the isothermal compression of one mole of Y, say, from the volume it occupied before reaction to the average volume it occupies after reaction, namely the average volume in the spherical shells around the X atoms. Each X, being the origin for locating a Y, can still be anywhere in V, so that the entropy change contains no contribution on account of the X's. It is of course immaterial which atom, X or Y, is taken as being at the center and which in the spherical shell. The important thing is that after reaction one mole of particles remains free to move in V, and one mole has been restricted to move in Nv. Nv is thus a free volume.

In spite of the fact that this type of calculation is not new,[10] we shall find it instructive to follow out its implications in detail, turning first to the meaning of the term $-\frac{1}{2}R$ in (7). The derivation shows that this is the sum of the $-R$ term in (1) and a $+\frac{1}{2}R$ which appeared in (6) from $T(d\ln\bar{A}/dT)$.

It is not difficult to recognize that the $-R$ is connected with what has been called the "communality"[2] of the volume V, and the "noncommunality" of the volume Nv. Communality

[9] J. E. Mayer and M. G. Mayer, footnote 1, Section 6g, pp. 135–138.

[10] Cf. for example, J. E. Mayer and M. G. Mayer, footnote 1, Section 9e, pp. 213–217.

has meant different things to different people, and part of the purpose of this paper is to discuss its significance. We shall therefore find it useful, to begin with, to consider what meaning can be given to it in clear-cut cases such as this one. In the nature of things, an X describing a volume v about a given Y cannot move into a second volume v about another Y without exchanging partners, or "places," with a second X. Exchanges can take place, in principle, by dissociation and recombination, so that every one of the N elements v is accessible to each X (or Y if we wished to consider the X's as centers). However, not all v's are accessible to all X's independently. On the other hand, before reaction the whole of V is accessible to each X independently. A configuration, for example, in which all the X's are to be found in one corner of V is very unlikely, but is not excluded, and makes its contribution to the partition function.

This is the meaning of the statement that the volume V is communal, whereas Nv is not.

As will appear later, it is permissible to associate this difference in communality with the term $-R$ in ΔS. Such a convention is useful in providing a physical interpretation for this term. Specifically, it gives a meaning to absorbing the $-R$ into the free volume, writing $V_f=Nv/e$ for an effective free volume, corrected to account for communality effects.[11]

The term $+\frac{1}{2}R$ in (6) is caused by the temperature variability of the free volume. The partition function for the vibrational motion can be written

$$Q_v=\frac{kT}{h\nu}=\frac{(2\pi\mu kT)^{\frac{1}{2}}}{h}\cdot 2\bar{A}, \tag{8}$$

where it appears in the form corresponding to a quasi-translational motion in one dimension, with a "volume" $2\bar{A}$. For a real one-dimensional translation, the partition function is

$$Q_1=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}l, \tag{9}$$

where l, the free length, or "volume" is an external parameter of the system, and is not temperature dependent. Physically this means that the length l available to any one particle is the same as is available to any other particle. This distinguishes l in (9) from $2\bar{A}$ in (8), for $\bar{A}$ is an average obtained from many A's, some large and some small. The variation between different A's may be regarded as a manifestation of the fluctuations which are characteristic of all systems in thermal equilibrium.

Mathematically, the temperature dependence of $\bar{A}$ makes a contribution to the entropy through the term $T(d\ln Q/dT)$ in the general statistical formula. Physically, the meaning of this extra entropy is to be found in the statement of Lewis:[12] "gain in entropy means loss of information." Strictly, for purposes of entropy interpretation, the idea of the volume of a gas has this meaning, and only this: when we have said that a molecule is in V we have stated accurately all that we know about its location. In the one-dimensional case, the entropy contains a term $R\ln l$, which means that we know the molecule is within a length of exactly l. In getting the entropy from (8) we obtain a term $R\ln(2\bar{A})$. But this as it stands tells more than we know, for it implies that each "particle" may be found in a length of exactly $2\bar{A}$, which is not true. To make it right we must say that on the average a "particle" is to be found in a length $2\bar{A}$, and, except on the average, we do not know how much larger or smaller the actual length is within which we must look for any individual "particle." This extra ignorance corresponds to extra entropy. How much extra entropy it corresponds to depends on what we know of the amount by which individual A's may differ from $\bar{A}$. The information we have on this, or the measure of our ignorance, is expressed in the proportionality between A and the square root of T. This leads, as shown above, to the term $+\frac{1}{2}R$ for the extra entropy. This term can also be incorporated into the effective free volume by multiplying the latter by $e^{\frac{1}{2}}$. This gives, for comparison with V, an effective free volume, corrected for communality and temperature dependence, $V_f=Nv/e^{\frac{1}{2}}$.

It remains to consider the term $R\ln F_e$. If more than one electronic state is involved for any

[11] This amounts to defining the free volume in a perfect gas as identical with the physical volume V. It would perhaps be more logical, but would be less convenient, to call the free volume in the gas Ve, and that in the "condensed" system Nv.

[12] G. N. Lewis, Science **71**, 569 (1930).

of the particles, and in particular if the electronic state of either atom, or of the molecule, is one in which there is a resultant angular momentum, appropriate terms must be added to the corresponding entropies.[13] We shall write the sum of these terms equal to zero. One special case which would give this is that in which the atoms are in ^1S states and the molecule is $^1\Sigma$. This is a very unlikely state of affairs for such a reaction as has been considered here. Our purpose, however, in discussing this reaction has been to establish a point of view for considering the condensation of a gas to a liquid or a solid. In such a process, changes in multiplicity of electronic states do not, in general, occur. We shall therefore omit the term $R \ln F_e$.

If the atoms X and Y happen to be identical, the treatment must be altered in two respects. First, in Q_{XY}, the symmetry number $\sigma(=2)$ must go into the denominator. Second, the factor V/N in the quotient Q/N, which occurs in the entropy expression, is only half as great for the atoms as for the molecule. The net result is to make

$$\Delta S = R\left[\ln\left(\frac{2Nv}{V}\right) - \tfrac{1}{2}\right] = R \ln \frac{2V_f}{V}. \quad (10)$$

Physically this corresponds to the fact that, since XX, XY, and YY are all the same, a given X can have as a partner not only any Y, but also any other X, making twice as many cells of volume v accessible to any bound atom.

We may sum up the results obtained thus far as follows: In the idealized reaction considered, at temperatures corresponding to classical excitation of all motions, the entropy change may be written in the form

$$\Delta S = R \ln \frac{V_f}{V}, \quad (11)$$

where V_f, the effective free volume of the bound atoms, equals the sum of the actual volumes of the cells in which these atoms are to be found, corrected for the effects of "communality" and of the variability of the cell sizes. Since the free volume of an atom in an ideal gas is the volume V, we may write

$$\Delta S = R \ln \frac{V_{f2}}{V_{f1}} \quad (12)$$

for the process.

A TRIATOMIC CONDENSATION

An exactly analogous calculation can be made for the reaction of three atoms X, Y, and Z to form a triatomic molecule XYZ. This can be carried through most easily in the special case of a linear triatomic molecule, with Y in the center, and with X and Z of equal mass and bound to Y so as to give equal restoring forces and equilibrium distances of separation from Y. CO_2, generalized to classical excitation of all the vibrations, is a case of this kind, and may be used as a model. We may omit symmetry considerations which arise due to the identity of the O atoms, having seen above that these produce no essential change in the things in which we are interested.

The calculations for this example have been carried through, using the necessary properties of and constants for the normal vibrations, which are again assumed to be of small amplitude, and simply harmonic. In order to outline the results, we let A_1 be the amplitude of the symmetrical mode, that in which the two oxygens move in and out symmetrically, the carbon remaining stationary. A_1 is defined in such a way that $r_{O-O} - r_{O-O} = A_1 \sin(2\pi\nu_1 t + \varphi_1)$. Likewise let A_2 be the amplitude of the unsymmetrical mode, that in which the C oscillates back and forth between the stationary oxygens, in the line joining them. Let A_y and A_z be the amplitudes for the bending modes, such that, for example, y, the distance through which the carbon is displaced in the Y direction out of the X axis (which contains the two oxygen atoms) is

$$y = A_y \sin(2\pi\nu_y t + \varphi_y),$$

a similar relation holding for z. Then it works out that ΔS for the association of the three atoms to form the molecule is given by

$$\Delta S = R \ln \left[\frac{4\pi r_{O-O}^2 \cdot 2\bar{A}_1 \cdot 2\bar{A}_2 \cdot 2\bar{A}_y \cdot 2\bar{A}_z \cdot N^2}{V^2} \right]. \quad (13)$$

[13] J. E. Mayer and M. G. Mayer, footnote 1, Section 6*i*, pp. 140–144.

The nuclear and electronic terms have been ignored as before. The absence of a numerical term in R is caused by cancellation (see below).

If we let $4\pi r_{O-O}^2 \cdot 2\bar{A}_1 = v_O$ and $2\bar{A}_2 \cdot 2\bar{A}_y \cdot 2\bar{A}_z = v_C$ then (13) becomes

$$\Delta S = R \ln \frac{Nv_O}{V} + R \ln \frac{Nv_C}{V}. \qquad (14)$$

v_O is the average volume of a spherical shell about one oxygen atom within which the other oxygen can be located after reaction. If one oxygen is taken as origin, the symmetrical vibration will carry the other oxygen in and out, as in the case of the diatomic molecule. This same vibration will also carry the carbon in and out and the rotation will carry it around on a spherical surface, but this motion of the carbon must be ignored in the entropy picture, and does not appear in the mathematical expression for the entropy. This corresponds to the fact that, for any given location of the outer oxygen in its shell, the position of the carbon, so far as it is governed by the rotation and the symmetrical vibration, is fixed. All of our ignorance of the orientation of the molecule, and of its state in respect to the symmetrical vibration, has been taken account of, and must not be counted again. The uncertainty which remains is of the position of the carbon between the two oxygens now thought of as fixed. Of this, all we know is that its center lies somewhere in a cubical box whose extension in the O−O line averages $2\bar{A}_2$, and which extends sidewise out of this line in the Y and Z directions by amounts which average $\bar{A}_y$ and $\bar{A}_z$, respectively, in both positive and negative senses.

The absence of a numerical term in (13) and (14) is caused by the fact that one dimension of the oxygen shell varies proportionally to $T^{\frac{1}{2}}$, and all three dimensions of the carbon box have this variation. This corresponds to extra entropy of $4\times\frac{1}{2}R$, which exactly compensates the $-2R$ caused by loss of communality of volume by one oxygen and the carbon. The inequality of distribution of temperature-variation entropy makes (14) deceptive, as it stands. To obtain effective free volumes for the C and O atoms which correspond correctly to the representation we have given of the CO_2 molecule, we must write

$$\Delta S = R \ln \frac{Nv_O}{Ve^{\frac{1}{2}}} + R \ln \frac{Nv_C e^{\frac{1}{2}}}{V} = R \ln \frac{V_{fO}}{V} + R \ln \frac{V_{fC}}{V}, \qquad (15)$$

that is, on our representation, V_f for the oxygen is smaller and V_f for the carbon is larger by a factor $e^{\frac{1}{2}}$ than N times the corresponding cell volume.

To complete the discussion of this special case we must now point out that while the foregoing treatment is consistent, and will give the correct value for ΔS, it is not unique. We could equally well have represented the CO_2 molecule as having the C atom free to move anywhere in V, with the two O atoms confined, respectively, to a spherical shell and a rectangular box. The result of this break-down is just as neat as the one in (15). It reads

$$\Delta S = R \ln \frac{V_{fO'}}{V} + R \ln \frac{V_{fO''}}{V}. \qquad (15')$$

If $V_{fO'}$ and $V_{fO''}$ are correctly evaluated (they will both be different from V_{fO} in (15)) ΔS will, of course, come out with the same value as before. The important point which this illustrates, and which we shall meet again later, is that we must not take too seriously the names by which it may be convenient to call individual contributions to an over-all entropy, or entropy change. Different ways of "taking apart" a given process may be useful for different purposes. They will all be equally "good" if they are carried through consistently and without error.

A GENERAL THEOREM

The cases which have been considered in detail above are of idealized molecules, and it is therefore important to recognize that they are examples of a theorem which is completely general so long only as all the motions involved are classically excited. This follows from the statistical definition of entropy as

$$S = k \ln \Omega, \qquad (16)^{14}$$

where Ω is the total number of possible states of

[14] J. E. Mayer and M. G. Mayer, footnote 1, Chapter 4.

the system compatible with the prescribed total energy. Where the motions are classical, Ω is the volume of phase space within which the representative point for the system may be without violating the assumed conditions. That is

$$\Omega=\frac{1}{N_1!N_2!\cdots N_s!h^{3t}}\times\int_{\text{region}}^{\text{accessible}}\cdots\cdots\int dp_1\cdots dq_t. \quad (17)$$

$N_1 \cdot N_2$, etc., are the numbers of the different kinds of atoms present, and $3t$ is the total number of degrees of freedom of the system, since t is defined as $N_1+N_2+\cdots+N_s$. The divisions by $N!$ and by h^{3t} take care, respectively, of the indistinguishability of the atoms and the scale in which the phase volume is to be measured.[15] It is an important property of this integral[14] that the same numerical result for its logarithm is obtained whether the integration is extended (a) over the states corresponding to the most probable distribution of energy for total energy in the range E to $E+dE$, (b) over all states in which the energy of the system lies within the range E to $E+dE$, or (c) over all states in which the energy of the system is equal to or less than E. If changes of the system in respect to nuclear spin orientation or of electronic state were of interest, a factor Ω_i, could be multiplied into the phase volume. For reasons already mentioned, we omit this.

For our purposes we may choose as the q's in (17) the Cartesian coordinates of the individual atoms, x_1, y_1, z_1, $x_2\cdots$, the p's being the components of momentum p_{x1}, p_{y1}, etc. Then the energy E is

$$E_q+E_{\text{int}}+\sum_{i=1}^{i=t}\frac{1}{2m_i}(p_{x_i}^2+p_{y_i}^2+p_{z_i}^2),$$

where E_q is the potential energy, a function of the instantaneous positions of all the atoms, and E_{int} is the sum of the internal energies of all the particles. By the principle of equipartition of energy[16] the sum of the p^2 terms is $\frac{3}{2}tkT$, which will be correct for any state of the system in which all the external motions of the atoms are classical. The integral over the p's in (17), therefore, is the hypervolume of the hyperellipsoid which is defined by

$$\sum_{i=1}^{i=t}\frac{1}{2m_i}(p_{x_i}^2+p_{y_i}^2+p_{z_i}^2)=\tfrac{3}{2}tkT.$$

This hypervolume is equal to

$$\prod_{j=1}^{j=s}(2\pi m_j kTe)^{3N_j/2}$$

(s = number of kinds of atoms present),

which makes

$$\Omega=\prod_{j=1}^{j=s}\frac{(2\pi m_j kTe)^{3N_j/2}}{N_j!h^{3N_j}}\times\int_{\text{compatible with } E}^{\text{all } x,\ y,\ z}\int dx_1\cdots dz_{N_s} \quad (18)$$

$$=\prod_{j=1}^{j=s}\frac{(2\pi m_j kTe)^{3N_j/2}}{N_j!h^{3N_j}}V_{fj}^{N_j}, \quad (19)$$

where $V_{f1}=\int dx_1dy_1dz_1$ (over all configurations compatible with E), etc.

(19) may be taken as defining the free volume of any atomic species as the geometrical mean (i.e., the N_jth root of the product) of the extensions of real space accessible to each of the N_j atoms of the kind in question, taken with due regard to compatibility of these extensions with each other and with the volumes accessible to all the atoms of other kinds.

The theorem which follows from (19) is that for any isothermal change of the system

$$\Delta S=S_B-S_A=k\ln\frac{\Omega_B}{\Omega_A}$$

$$=N_1k\ln\left(\frac{V_{fB}}{V_{fA}}\right)_1+N_2k\ln\left(\frac{V_{fB}}{V_{fA}}\right)_2+\cdots, \quad (20)$$

or, per mole of each kind of atom, ΔS has a contribution R times the natural logarithm of the ratio of its free volume after the change to that before. This is a direct consequence of the equipartition of energy, which makes the factors preceding the V_f's in (19) cancel out if the temperature is held constant.

[15] J. E. Mayer and M. G. Mayer, footnote 1, Chapter 2.
[16] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Section 332, pp. 121–123.

For the special case of a perfect gas, $V_f = V$, and for a mixture of perfect monatomic gases (19) gives for each constituent a factor of

$$\Omega_g = \frac{(2\pi mkTe)^{3N/2}}{N!h^{3N}} V^N \tag{21}$$

in Ω or a molal entropy of

$$k \ln \Omega_g = R\left[\ln \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot \frac{V}{N} + \frac{5}{2}\right]$$

as it must.

For the special case of a diatomic molecule such as the molecule XY considered to begin with, the evaluation of Ω is more conveniently carried out in terms of Cartesian coordinates for the center of gravity of the molecule, and polar coordinates for the relative positions of the atoms. The transformation to these coordinates involves introduction of reduced masses, and also gives momenta in such a form that E_p contains the coordinates also, e.g.,

$$\epsilon_{p_1} = \frac{p_{r_1}^2}{2\mu_1} + \frac{p_{\theta_1}^2}{2\mu_1 r_1^2} + \frac{p_{\varphi_1}^2}{2\mu_1 r_1^2 \sin^2 \theta_1}. \tag{22}$$

This results in an expression for Ω which does not lend itself in the intermediate stages to separation in such a form as (18). However, (19) is still correct for expressing the final value of the integral, which is

$$\Omega = \frac{(2\pi m_x kTe)^{3N/2}(2\pi m_y kTe)^{3N/2} e^{N/2}}{N!h^{6N}} \times V^N \left[4\pi r_0^2 \cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right]^N. \tag{23}$$

(23) with (21) gives

$$\frac{\Omega_{XY}}{\Omega_X \Omega_Y} = \frac{N!\left[4\pi r_0^2 \cdot 2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right]^N e^{N/2}}{V^N}, \tag{24}$$

or

$$\Delta S = k \ln \frac{\Omega_{XY}}{\Omega_X \Omega_Y} = R\left[\ln\left(\frac{Nv}{V}\right) - \tfrac{1}{2}\right] \tag{25}$$

as before (Cf. (6)), using v again for the volume of the spherical shell.

The existence of this general theorem shows that of all the restrictive assumptions made in obtaining Eqs. (2)–(7), and (13)–(15), the only essential one was that of classical excitation of the motions. If the vibrations had not been assumed small, nor harmonic, the mathematics would have become enormously more complicated, but a result of the same form (20), with the same physical meaning of V_f, must still have been obtainable in principle.

Since there are very few systems of physical interest in which all of the motions are classically excited, it is important to note that all of the results of this section hold for any classical part of the motion of a system if the remaining motions, classical or non-classical, can be assumed to be separable from the motion of interest, and not to change during the process under discussion. For Ω, as a total number of states, can be represented as a product of numbers of "sub-states" for the various modes of motion in which the energy is separable. In particular, for the external (translation) and internal (electronic, rotation, vibration, and internal rotation) motions of a system of molecules, Ω may be written

$$\Omega = \Omega_e \cdot \Omega_i. \tag{26}$$

Then if in a change from state A to state B, Ω_i is unchanged,

$$\Omega_B / \Omega_A = \Omega_{eB} / \Omega_{eA}. \tag{27}$$

Since the external motions of the molecules in gases and liquids can be taken as classical, it is therefore always permissible to write

$$\Delta S = R \ln \frac{V_{fB}}{V_{fA}} \tag{28}$$

for the part of the entropy change associated with motions of the molecular centers of gravity, so long as these are separable from the internal motions. We have shown that the free volumes suitable for use in (28) are real physical volumes which can be interpreted in terms of a physical picture. We have also shown, however, that the physical picture must be sufficiently refined to include a correct interpretation of communality and of the temperature dependence of cell volumes.

POLYATOMIC LIQUIDS

Since we shall want, in the following paper, to use (28) in discussing the entropy change which accompanies the condensation of a gas to a liquid, we may pause here to consider how nearly this process fulfills the conditions of validity of (28), and what can be done in cases where it does not. We shall see later that in most real liquids the internal motions are not, in fact, as free as in their vapors. As it stands, therefore, (28) will not give ΔS of condensation correctly. However, the method used to derive (28) also provides a means of generalizing it, since in a number of important cases the significant interference with internal motions concerns rotation only. This follows from the fact that the positions of Raman lines and infra-red bands are not greatly changed in passing from the vapor to the liquid state, which means that the vibrations are, to a good approximation, not changed in frequency, or that the vibrational motions are not greatly perturbed. The broadening of the lines, or of the bands, on condensation is caused entirely by changes in the rotational energy differences which add to, or subtract from, the changes in vibrational energies which are being measured.

Now for all ordinary polyatomic molecules, the rotational motion is effectively classical. Therefore, proceeding along lines suggested by the pseudo-CO_2 case above, we can make a generalized Ω, and obtain a "complete" free volume for carbon tetrachloride, for example, which consists of the "ordinary" free volume of the molecular center of gravity, multiplied by the volume of the spherical shell containing one of the chlorine atoms, by a ring volume for a second chlorine, and by a box volume for each of the other two chlorines. The effective thickness of the spherical shell and the effective linear dimensions of the other volumes cannot be obtained by the methods so far employed, for the vibrational motions which determine them are not classical. This is of no importance for our purpose, however, as these non-classical quantities may be assumed, as just stated, to be unchanged by the condensation process, and will cancel out. The volume of the spherical shell, for CCl_4 vapor, is $4\pi r_0^2\Delta r$ as before, Δr being the effective thickness provided by the (quantized) breathing mode of vibration. The volume of the ring or "doughnut" is $2\pi r_0 \sin\theta wt$ where w is the effective width and t the effective thickness, determined, respectively, by specified bending and unsymmetrical valence vibrations. θ is the (constant) tetrahedral angle which determines the equilibrium inclination between the valence bonds from the carbon to the shell and ring chlorines. Then $4\pi r_0^2\Delta r \cdot 2\pi r_0 \sin\theta wtb_1b_2$ is the supplementary free volume which is to be multiplied into the ordinary free volume of the center of gravity to make the complete free volume, b_1 and b_2 being the effective volumes of the boxes occupied by the other chlorines.

When condensation takes place, and the rotation is no longer free, the chlorine which was chosen to move in the shell is now confined, on the average, to a restricted area on its surface, an area measured by s, the solid angle it subtends at the carbon center. The chlorine which was chosen to move in the ring is, at the same time, confined, on the average, to a restricted segment of it, a segment measured by the angle a it subtends at the planar center of the ring. The supplementary free volume is thus reduced to $sar_0^3 \sin\theta wt\Delta rb_1b_2$, all the factors except s and a being unchanged.

(28) is therefore generalized to

$$\Delta S = R \ln \frac{V_{fl} sar_0^3 \sin\theta\Delta rwtb_1b_2}{V_{fg} 8\pi^2 r_0^3 \sin\theta\Delta rwtb_1b_2} = R \ln \frac{\gamma V_{fl}}{V_{fg}}, \quad (28')$$

where V_{fl} and V_{fg} have the same meanings as before. γ equals $sa/8\pi^2$ and is the "free angle ratio" of Kincaid and Eyring.[17] It is the average fraction of the total free rotational motion which the molecule is still able to execute after condensation. It is clear that $\gamma \leqslant 1$.* The fact that the symmetry number of CCl_4 is 12 affects both numerator and denominator of γ in the same way, and means, merely, that the 12 equivalent positions in which a CCl_4 can be caught by a snapshot of its rotation in the gas, or in which it can oscillate against its neighbors in the liquid, count as one only.

(28′) is rigorous, with the physical meaning we have given, so long, and in so far as, (a) the internal vibrational motions are actually separable from the translation and rotation of the molecule, (b) the internal vibrational motions of the molecule are not changed by the presence of neighbors, and (c) the oscillations which have replaced rotation in the liquid are effectively classical. It is probable that none of these conditions is exactly fulfilled, but it is also probable that none of them fails badly enough to discourage the use of (28′) for CCl_4. CCl_4, however, is an especially favorable case among real liquids. A treatment corresponding to that just given can of course be written down for any polyatomic liquid. But for long chain molecules, such, for example, as *n*-octane, it is likely that some intramolecular bending and torsional vibrations will interact with the translational and rotational vibrations of the whole molecule in the liquid in such a way that it will be impossible to calculate, or even to visualize separately, γ and V_f, as they appear in (28′). Formally (28′) will still mean what it purports to if the product γV_f is considered as a single quantity. But the treatment used later on, in which V_f for a liquid is calculated separately from a cell or cage model, will lose its clarity of outline in proportion as this difficulty becomes more acute.

Before attempting a complete analysis of so complicated a system as a polyatomic liquid, it will be necessary to explore additional simple cases upon which we may base a point of view and method.

COMMUNALITY IN A ONE-DIMENSIONAL SYSTEM

A model of a hard-sphere one-dimensional gas has been considered by Tonks,[18] and an analysis

[17] J. F. Kincaid and H. Eyring, J. Chem. Phys. **6**, 620 (1938).

* The effective γ will presumably be larger than the geometrical picture would suggest, due to the effect of fluctuations.

[18] L. Tonks, Phys. Rev. **50**, 955 (1936).

of the small vibrations of a one-dimensional crystal suitable for our purposes is given by Mayer and Mayer.[19] The utility of these treatments in discussing communal entropy has been pointed out by Rice.[20] We shall repeat some of Rice's calculations, but shall arrive at results somewhat divergent from his.

Tonks[18] in effect evaluates the configuration integral for a one-dimensional gas of N molecules of a "hard" diameter σ, confined in a length l. It is assumed that when two molecular centers are farther apart than σ no force operates between the molecules. His result, for very large N, is

$$I=\frac{1}{N!}[l(1-\theta)]^N, \tag{29}$$

where θ is the fraction of the length occupied by the molecular diameters or $\theta=N\sigma/l$. This can be made into a classical (not yet normalized) phase integral, by multiplying by the momentum integral $(2\pi mkT)^{N/2}$, giving

$$Q'=\frac{(2\pi mkT)^{N/2}}{N!}[l(1-\theta)]^N. \tag{30}$$

The $N!$ in the denominator arises mathematically from the successive integration N times of an xdx in the configuration integral. Tonks points out that corresponding to the $N!$ serial orders in which N molecules, assumed to be distinguishable, can be arranged in line there are actually $N!$ equivalent regions of configuration space, of which (29) represents integration over only one. He justifies the restriction to one region by the fact that in a one-dimensional gas the molecules are unable to pass each other. This leads to the right result, but we wish to approach it differently. If Tonks' result is to be used physically it must lead to a partition function for a phase which could stand in equilibrium with other phases, so that "evaporation" and "recondensation" would enable any order to be realized, still imagining the particles to be distinguishable. The physical possibility or impossibility of interchanges in the linear gas is therefore irrelevant.[21]

To obtain the correct phase integral for the assumed system we must therefore multiply (30) by $N!$ before normalization. Normalization, in Boltzmann statistics, consists in dividing by h^N for unit of "volume" in phase space, and by $N!$ for the indistinguishability of the molecules,[15] and yields the correct partition function for the assembly as a whole

$$Q=\frac{(2\pi mkT)^{N/2}}{N!h^N}[l(1-\theta)]^N, \tag{31}$$

in agreement with Rice and, mathematically, with Tonks. As θ approaches zero, this approaches

$$Q=\frac{(2\pi mkT)^{N/2}}{N!h^N}l^N \tag{32}$$

in exact analogy with the expression for a perfect (three-dimensional) gas as a whole:

$$Q=\frac{(2\pi mkT)^{3N/2}}{N!h^{3N}}V^N. \tag{33}$$

The molal entropies corresponding to (31), (32), and (33) are given by the general formula

$$S=k\left[\ln Q+T\frac{d\ln Q}{dT}\right],$$

or, for (31)

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{1}{2}}}{h}+\tfrac{1}{2}+\ln\frac{l(1-\theta)}{N}+1\right], \tag{34}$$

and for (33)

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}+\tfrac{3}{2}+\ln\frac{V}{N}+1\right]. \tag{35}$$

In each of these cases, the formula has been arranged so that there is a volume contribution to the entropy corresponding to a cell volume,

$$R\ln(V/N) \quad \text{or} \quad R\ln[l(1-\theta)/N],$$

plus an R which comes from the Stirling approximation for $N!$. As we have seen this is commonly called a communal entropy, and associated with the volume contribution. Logically it occurs along with $\ln N$ and is associated with V only as we choose to consider V and N together as the ratio V/N. From this point of view, the suggestion of

[19] J. E. Mayer and M. G. Mayer, footenote 1, Section 11*f*, pp. 246–248.
[20] O. K. Rice, J. Chem. Phys. **12**, 1 (1944).
[21] Cf. E. D. Eastman and R. T. Milner, J. Chem. Phys. **1**, 444 (1933).

Rice[20] that a three-dimensional solid or liquid constructed in analogy with Tonks' one-dimensional gas or liquid should have a communal entropy of $3R$ is seen not to be correct. For the analog of (31) becomes

$$Q=\frac{(2\pi mkT)^{3N/2}}{N!h^{3N}}[l(1-\theta)]^{3N}, \tag{36}$$

the $N!$ appearing to the first power as before, this being the necessary and sufficient way of accounting for the indistinguishability of the N molecules present.[15] This gives

$$S=R\left[\ln\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}+\tfrac{3}{2}+\ln\frac{[l(1-\theta)]^3}{N}+1\right], \tag{37}$$

as the superficially straight-forward generalization of (34) to three dimensions. Results obtained below suggest, however, that a straight-forward theoretical treatment of the 3-dimensional hard-sphere problem cannot be attained so simply except where θ is very small. Physically, the results for real crystals support Rice's idea that solids should have rather large amounts of entropy which may be called communal.

THE LINEAR CRYSTAL

The case of the linear monatomic crystal treated by Mayer and Mayer differs from Tonks' problem in that here the atoms of the crystal are bound to each other so that any displacement of one of them produces a force on its neighbors. The minimum of potential energy is assumed to correspond to equal separations of a units between all pairs of neighbors. The length of the crystal is thus $(N-1)a$ for N atoms. The displacement of the i'th atom is called ξ_i, and for small vibrations

$$E=E_0+\tfrac{1}{2}f\sum_{i=1}^{N-1}(\xi_{i+1}-\xi_i)^2.$$

For N very large, and the two end atoms assumed to be held fixed, it is shown that there are $N-2$ normal modes, such that the frequency of the n'th is

$$\nu_n=\frac{1}{\pi}\left(\frac{f}{m}\right)^{\frac{1}{2}}\sin\frac{\pi n}{2(N-1)}\qquad 1\leqslant n\leqslant(N-2), \tag{38}$$

m = mass of one atom. Since N is very large, this makes $\nu_{\max}$, the highest possible frequency, (sensibly ν_N)

$$\nu_N=(1/\pi)(f/m)^{\frac{1}{2}}. \tag{39}$$

This is easily shown to correspond to the mode in which neighboring atoms vibrate "against" each other, such that $-\xi_i=\xi_{i+1}=\xi_{i-1}$. The motion is described by $\xi_i=\pm A_N\sin(2\pi\nu_N t+\varphi)$, + sign for odd i, − sign for even i, i.e., the amplitude constant for the mode also describes the separate harmonic motion of each atom.

The method employed in the discussion following (6) can be used to obtain the average value of A_N in classical thermal equilibrium, and yields $\bar{A}_N=\frac{1}{2}(\pi kT/2Nf)^{\frac{1}{2}}$. The appearance of N in the denominator makes $\bar{A}_N$ a very small length even on an atomic scale. It is therefore of greater interest to consider another length, the average amplitude within which the atoms would vibrate if only this mode were excited, but the average energy of the crystal were NkT— i.e., if all of its actual equilibrium energy were concentrated in this one mode of highest frequency. This supposition corresponds to picturing the crystal as a sort of specialized Einstein solid, in which all of the virtual oscillators not only have the same frequency, but are reinforcements of a single actual normal mode of the crystal. The average value of A_N for such excitation may be called $\bar{A}_E$, and is given by

$$\bar{A}_E=\tfrac{1}{2}(\pi kT/2f)^{\frac{1}{2}}. \tag{40}$$

The partition function (classical) for the crystal is

$$Q=\prod_{n=1}^{N-2}(kT/h\nu_n), \tag{41}$$

so that

$$\ln Q=\sum_{n=1}^{N-2}\ln\frac{kT}{h\nu_n}$$

$$=N\ln\frac{kT}{h}-\int_0^N\ln\nu_n dn, \text{ sensibly.} \tag{42}$$

Integration gives

$$\ln Q=N\ln\left[\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\left(\frac{\pi kT}{2f}\right)^{\frac{1}{2}}\right] \tag{43}$$

$$=N\ln\left[\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\bar{A}_E\cdot 2\right]. \tag{43'}$$

For a crystal,

$$S=k\left[\ln Q+T\frac{d\ln Q}{dT}\right],$$

so that for this crystal

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}2\bar{A}_E\right\}+\ln 2+1\right]. \quad (44)$$

Now $2\bar{A}_E$ is a "natural" cell size to take for the vibration of an atom in this crystal, since if the crystal were vibrating with all of its energy in its mode of highest frequency the motion of each atom would in fact be confined to such a cell. Moreover, such a cell can be assigned to each atom without any overlapping, and with none of the length of the crystal left unaccounted for. If this identification is made, (44) shows that the crystal has a communal entropy of $R\ln 2$. As compared with (34) it also has an extra entropy of $(1/2)R$ caused by the temperature variation of $\bar{A}_E$.

Rice[20] considers a different "natural" cell, corresponding to the vibration of the i'th atom when atoms $i+1$ and $i-1$ are held fixed. It is easy to show that, for this mode, $\nu_F=1/2\pi(2f/m)^{\frac{1}{2}}$ or

$$\bar{A}_F=(\pi kT/2\cdot 2f)^{\frac{1}{2}}=\frac{1}{\sqrt{2}}(\pi kT/2f)^{\frac{1}{2}} \quad (45)$$

this makes

$$\bar{A}_F=\sqrt{2}\bar{A}_E, \quad \text{or} \quad 2\bar{A}_E=\sqrt{2}\bar{A}_F. \quad (46)$$

It is, again, "natural," to assign a cell of length $\bar{A}_F$ to each atom, for if each one is given this length extending, say, in the direction of positive x, the whole length of the crystal can once more be thought of as accounted for without overlapping. Taking this interpretation, we get

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\bar{A}_F\right\}+\ln(2\sqrt{2})+1\right], \quad (47)$$

in agreement with Rice. This would make the communal entropy $\frac{3}{2}R\ln 2$.

This example is instructive as illustrating the essentially arbitrary nature of the whole idea of cells and of communal entropy. The actual entropy of the crystal, from (43) is

$$S=R\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\left(\frac{2\pi kT}{f}\right)^{\frac{1}{2}}\right\}+1\right], \quad (48)$$

and even here the argument of the logarithm has been taken apart into factors in a way which can be justified only on grounds of convenience. Such forms as (44) and (47) can have the same justification, but neither is unique. If we may say so, the crystal itself does not know that its atoms move in cells, nor what size the cells should be. Correspondingly, it does not know how much of its entropy is communal, and how much should be called by other names.

In fact, it is not necessary to use the idea of communal entropy in condensed phases at all if the cell sizes are chosen, as they could be, to account exactly for the whole entropy without leaving any residue. In gases also, the idea of communality of volume could be dispensed with, since the term R in the entropy need not be associated with the volume contribution; as shown above, it arises from $\ln N!$ and $N!$ is introduced to account for the indistinguishability of the molecules. We shall continue to use communal entropy as a working tool, however, since it gives us a way of making rather good estimates of thermodynamic entropies from physical considerations involving cell sizes. To complete our discussion of it we now proceed to show that it is possible to think of gases and condensed phases as being fundamentally the same in the communality which they display.

FLUCTUATION ENTROPY

In assigning a cell volume $2\bar{A}_E$ in the linear crystal we are asserting that while we know that an atom is in its cell, we do not know its position inside the cell. In assigning such a cell to each atom, we assert that after we have located one atom in its cell (purchasing this knowledge at the price of the term $k\ln(2\bar{A}_E)$ in the entropy) we still know nothing of the location within their cells of any of the other atoms. If only the one mode of vibration were excited, however, as in the pseudo-Einstein picture above, this would not be true, for in that mode the phases and amplitudes of all the ξ_i are related. From this point of view, then, the effect of the distribution of frequencies and wave-lengths is to destroy the correlation of phase between the motions of the

TABLE I. The fluctuation factor α in monatomic crystals.

Substance	M	Θ	T°K	P_{mm}	$\Delta H_{cal./mole}$	$\log \alpha$	α
Argon	39.94	80[k]	77.48	200.6[b]	1880[a]	0.63	4.25
Krypton	83.7	63[k]	102.63	110.98[c]	2540[a]	0.89	7.76
Xenon	131.3	55[j]	143.2	132.2[d]	3850[a]	0.39	2.45
Magnesium	24.32	290[h]	734.8	2.27×10^{-2} [e]	35,300[a]	0.25	1.78
Zinc	65.38	235[i]	619.0	7.76×10^{-3} [e]	30,200[a]	0.77	5.89
Cadmium	112.41	168[i]	523.0	4.82×10^{-3} [f]	26,420[a]	0.72	5.25
Mercury	200.6	97[i]	223.1	4.5×10^{-7} [g]	15,210[a]	0.75	5.62

[a] K. K. Kelley, Bull. 383, U. S. Bureau of Mines, Washington, 1935.
[b] F. Born, Ann. d. Physik. **69**, 473 (1922).
[c] W. H. Keesom, J. Mazur, and J. J. Meihuizen, Physica **2**, 669 (1935).
[d] K. Peters and K. Weil, Zeits. f. physik. Chemie **A148**, 27 (1930).
[e] F. F. Coleman and A. Egerton, Phil. Trans. Roy. Soc. **A234**, 177 (1935).
[f] A. Egerton, J. Chem. Soc. **123**, 3024 (1923).
[g] A. Eucken, Landolt-Bornstein *Physikalisch-chemische Tabellen* fifth edition Supp. II b, p. 1292.
[h] F. Simon, Landolt-Bornstein *Physikalisch-chemische Tabellen* fifth edition Supp. II b, p. 1232.
[i] Fowler and Guggenheim, *Statistical Thermodynamics*, p. 145.
[j] K. Clusius and L. Riccoboni, Zeits. f. Physik. Chemie **B38**, 81 (1937).
[k] K. Clusius, Zeits. f. physik. chemie **31B**, 459 (1936).

atoms in this one mode. Another effect is to produce motions—surgings, swayings, or fluctuations—of the center of the cell, enabling whole sections of the crystal to encroach on each other. This produces communal entropy, i.e., entropy associated with the non-exclusiveness of the cells.[22] On the face of it this seems to be different in kind from the communal entropy in a gas, where the molecules are assigned such large cells that many molecules (for a perfect gas an infinite number of them) can be in one cell. A little reflection shows, however, that, whether in a gas, a liquid, or a crystal, the occasion for considering communal entropy arises only because of the occurrence of fluctuations in density, and that the communal entropy we have described for a crystal is really the same thing as is found in a gas.* We therefore propose the name *fluctuation entropy* as an alternative for the term communal entropy. Our earlier discussion of the entropy contribution due to temperature variability of cell-size shows that this is also a fluctuation entropy. Since in crystals the temperature variability of cell size and the encroachment of one atom upon another are not independent, we shall use the term fluctuation entropy to refer to the extra entropy from whatever "cause," which must be added to cell-volume entropies as calculated from models.

[22] Cf. O. K. Rice, J. Chem. Phys. **6**, 476 (1938).

* This is paradoxical from the point of view adopted in discussing (7). The paradox can be resolved by remembering that it is only "free volume" which is shared in condensed phases, and all of the free volume is accessible for sharing. In a gas (practically) the whole volume is free volume.

REAL CONDENSED SYSTEMS

Our program now calls for the application of the ideas developed in the foregoing sections to real systems. We shall find that the study of simple real systems (crystals) fills enough of the remaining gaps in the picture to provide a representation which can be used with some confidence for complicated real systems (liquids), with the purpose of deriving, or interpreting, relationships connecting entropy changes with other experimental quantities and with the known structural features of individual substances.

As a suitable starting point, we may consider the process of vaporization of a liquid or a solid. From (28′) the molal entropy change may be written

$$\Delta S = R \ln (V_{fg}/\gamma V_{fc}), \tag{49}$$

V_{fg} being molal free volume in the gas and V_{fc} that in the condensed phase. Subject to the conditions previously discussed, (49) is a general equation.

For practical purposes, and unless otherwise noted, we absorb into γ the difference (usually small in the cases of interest) between the actual entropy of the vapor (saturated or not) and that of the same substance reduced to a suitable standard state as a perfect gas, writing

$$\Delta S = R \ln (V_g/\gamma V_{fc}). \tag{50}$$

There are now several possible paths which might be followed. One, which exemplifies the way in which the method can be used, is to

write, for an *equilibrium* vaporization,

$$\ln (V_g/\gamma V_{fc}) = \Delta S/R = \Delta H/RT,$$
$$V_g/\gamma V_f = RT/P_g\gamma V_f = e^{\Delta H/RT}, \quad (51)$$
$$P_g = RT/\gamma V_f e^{-\Delta H/RT}.$$

MONATOMIC CRYSTALS

Equation (51) (without γ) for the vapor pressure of a condensed phase has been derived by various writers[3] by methods essentially equivalent to the one employed here. In principle, it may be applied in any case for which estimates of V_f and γ can be made. We shall use it, with data for the solid-vapor equilibrium for some monatomic solids, to complete our free volume picture.

As a first step in obtaining V_f for a monatomic crystal one can take (43′) for ln Q for the linear crystal, and multiply by 3 to get ln Q for a three-dimensional crystal in which the motions in the three directions are independent of each other. This gives

$$\ln Q = N\left[\ln\left\{\frac{(2\pi mkT)^{\frac{1}{2}}}{h^3}\right\} + \ln (2\bar{A})^3 + \ln 8\right]. \quad (52)$$

Here $N\cdot(2\bar{A})^3\cdot 8$ is a free volume. We have seen, however, that even in the linear case the interaction of the atomic motions introduces some arbitrariness in the magnitude of the fluctuation entropy to be added. The best we can hope to do here, therefore, is to write

$$2\bar{A}' = (\pi kT/2f')^{\frac{1}{2}} = \frac{1}{\nu}(kT/2\pi m)^{\frac{1}{2}} \quad (53)$$

for some frequency ν and substitute for the ln 8 in (52) a term ln α, using the disposable constant α to represent the fluctuation factor appropriate to the choice of ν which defines the cell size. α will also, as used here, be appropriate to the implied cubic cell shape. It is partly our ignorance of what effective shape a cell should have which requires the use of a disposable constant.

We can guess that, for a plausible choice of ν, α will be of order of magnitude unity. Remembering that V_f is made up of "full" cells and therefore should have an e in the denominator, in analogy with (7′), and that $(\bar{A}')^3$ is proportional to $T^{\frac{1}{2}}$, we may write

$$V_f = N\left[\frac{1}{\nu}(kT/2\pi m)^{\frac{1}{2}}\right]^3 \alpha e^{\frac{1}{2}}. \quad (54)$$

Since for a monatomic vapor, at low pressure, γ must be very nearly equal to 1, this converts (51) to

$$P = \frac{(2\pi m)^{\frac{1}{2}}\nu^3}{(kT)^{\frac{1}{2}}\alpha e^{\frac{1}{2}}} e^{-\Delta H/RT} \quad (55)$$

for the vapor pressure of the crystal, a form identical, except for the factor $\alpha e^{\frac{1}{2}}$, with one given in 1903 by Mie[23] for liquids.

For ν we may choose a Debye characteristic frequency calculated from heat capacity data (for some one temperature). The physical meaning of this choice cannot be stated precisely, since we do not know the true distribution of frequencies in the solid,[24] and, therefore, cannot tell just what kind of an average the Debye treatment represents. This sort of uncertainty is already provided for in α. We may also allow α to take up whatever uncertainty is introduced through the necessity of using for m an average over the masses of the various isotopic species which may be present.

Except for α, (55) is now a relation between experimental quantities, and there are a number of substances for which the necessary data exist for a calculation of α. In Table I appear the results of such a calculation for some crystalline elements which are volatile enough to permit the experimental measurement of vapor pressures. Writing $h\nu = k\Theta$, (55) gives

$$P = \frac{(2\pi)^{\frac{1}{2}}k^{5/2}}{N^{\frac{1}{2}}h^3e^{\frac{1}{2}}}\cdot\frac{M^{\frac{1}{2}}\Theta^3}{T^{\frac{1}{2}}}\cdot\frac{1}{\alpha}\cdot e^{-\Delta H/RT} \quad (55')$$

where N = Avogadro's number and M is the conventional atomic weight. This gives

$$\log \alpha = \log\left[\frac{M^{\frac{1}{2}}\Theta^3}{PT^{\frac{1}{2}}}\right] - 0.4343\frac{\Delta H}{RT} + \log C,$$
$$\log C = \log\left\{\frac{(2\pi)^{\frac{1}{2}}k^{5/2}}{N^{\frac{1}{2}}h^3e^{\frac{1}{2}}}\right\} \quad (56)$$

and takes the value 1.0723, if P is in millimeters of mercury.

[23] G. Mie, Ann. d. Physik 11, 657 (1903).
[24] E.g., M. Blackman, Proc. Roy. Soc. London **A159**, 416 (1931); E. W. Montroll, J. Chem. Phys. 11, 481 (1943).

It is observed that the values of α cluster around 5. This corresponds to fluctuations in position of the unit cells which have the effect of making each linear dimension greater by a factor of $5^{\frac{1}{3}}=1.71$ than it would be if the cells were stationary. The exact numerical values of α cannot be interpreted nor compared without more discussion than we propose to give here. We may point out, however, that (55′), with the thermodynamic requirement $d\ln P/dT=\Delta H/RT^2$, contains a relation between the temperature variations of α, Θ, and ΔH. Although we have computed α at random temperatures, it is of interest to consider the orders of magnitude of the various quantities in the picture. These can be seen by calculating

$$2\bar{A}'=\frac{T}{\Theta}\cdot\frac{hN}{(2\pi MRT)^{\frac{1}{2}}}=\frac{1.59\times10^{-3}}{(MRT)^{\frac{1}{2}}}\cdot\frac{T}{\Theta}.$$

For argon, at the temperature used above, $2\bar{A}'=3.04\times10^{-9}$ cm. In solid argon, the distance apart of two alternate atoms[25] (which form the "boundaries" of the box containing the one between them) is 7.68A. This means that the "free length" for an atom is $0.304/7.68\times100=4.0$ percent of the internuclear distance of its "wall" neighbors. Multiplication by $\alpha^{\frac{1}{3}}$ gives 4.93×10^{-9} cm or 6.47 percent of the wall-to-wall distances. $V_f=\alpha e^{\frac{1}{3}}(2\bar{A}')^3\times6\times10^{23}=0.118$ cc. Since the molal volume of the solid is about 22.4 cc, $V_f/V_s=0.00525$. For cadmium at the temperature used $2\bar{A}'=2.24\times10^{-9}$ cm or 3.8 percent of one of the wall-to-wall distances. With fluctuations (multiplied by $\alpha^{\frac{1}{3}}$) this becomes 6.6 percent. $V_f=.0588$ cc and $V_f/V_s=0.00453$.

These numbers all seem reasonable, and support the idea that some real significance attaches to the picture we have developed of the free volume in a solid.

[25] *International Critical Tables*, Vol. I, p. 340.

An approach to the solid state which is more reminiscent of the conventional one can be made by substituting (53) into (52), and using

$$h\nu=k\Theta \quad \text{and} \quad S=R\left[\ln Q+T\frac{d\ln Q}{dT}\right].$$

This gives

$$S_c=R\left[\ln\left(\frac{T}{\Theta}\right)^3+\ln\alpha+3\right], \qquad (57)$$

where α has the same meaning as before. (57) becomes equal to the high temperature limit for S for the Einstein solid if $\alpha=1$, and for the Debye solid if $\alpha=e$.[26]

A fuller discussion of this and other points involved in a free volume treatment of solids must be left for a separate paper. We may recall here, however, that α as we have evaluated it depends on the way in which we chose to define the cell volume available to an atom. Our choice corresponded to (44) for the one-dimensional case. If we had taken Rice's choice (Cf. (46) (47)) the cell would have been smaller, and α larger, by a factor of $2^3=2.828$, giving values in the neighborhood of 14. This is still smaller than the communality factor $e^3=20.0855$ proposed by Rice[22] for a solid of hard elastic spheres. It will be observed, however, that we have adopted the physical idea of communality in solids which, so far as the writer is aware, Rice was the first to propose.[20] His qualitative idea that, with "natural" choices of cell volumes in both cases, fluctuation entropies in solids will, in general, be larger than those in gases (where $\alpha=1$, by our conventions) is also confirmed by the numerical results we have obtained. In the following paper it will be found that liquids (again, for a "natural" definition of cell volume) fall between solids and gases in this respect.

[26] Cf. J. E. Mayer and M. G. Mayer, footnote 1, p. 322.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 11 NOVEMBER, 1945

Free Volume and Entropy in Condensed Systems

II. Entropy of Vaporization in Liquids and the Pictorial Theory of the Liquid State

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The results of the first paper of this series, and a generalization of a method due to Eyring, are used to obtain an expression for the free volume of a liquid, $V_f = fb^3g^3/h^3n^3 \times [RT/\Delta E_v]^3$, and an equation for the entropy of vaporization. $\Delta S = R[\ln V_g - \ln V_l - \ln \beta + 3 \ln (\Delta H/RT - 1)]$. Here $\beta = \gamma fb^3g^3/h^3n^3$, where γ measures the interference in the liquid with the internal motions (rotations, vibrations) of the molecule, and f, b, g, h, n are quantities which depend on the geometry of the liquid and the energetic and dynamic interaction of the molecules. The rule of Barclay and Butler, that the 25°C value of ΔS for various pure liquids has a rough linear relationship to the corresponding ΔH of vaporization, is shown to imply a general tendency for a liquid to have a smaller β the larger its ΔH of vaporization. In many cases this means a smaller γ, resulting from increased interference with rotation of the molecules in the liquid. Pitzer's perfect liquid has a value $\beta = 16$, sensibly independent of ΔH. This is taken to mean that in such a liquid as benzene or carbon tetrachloride ($\beta \approx 6$) the interference with free rotation is considerable. For CS_2 there is evidence that the intermolecular force field differs from "normal," and the difference in potential function between liquid metals and normal liquids shows up strongly. Accepting the value $\beta = 16$ found for the ideal liquid as a norm, it is proposed to call $R \ln (16/\beta)$ for any liquid the hypothetical entropy defect (HED) and interpret it as the amount by which the entropy of the liquid (referred to the same substance as a perfect gas) is less than that of the ideal liquid in the "corresponding" state.

INTRODUCTION

IN the preceding paper[1] (hereinafter to be referred to as I) it was shown that, by relating it to entropy changes, the free volume of a condensed system may be determined in a usefully exact way. It was also shown that the free volume so determined bears a usefully exact relationship to a pictorial free volume based on cells or cages in which the center of gravity of a molecule is "free" to move. The latter result can be expressed in the equation

$$V_f = Nvf, \qquad (1)$$

where V_f is the molal free volume, v is the average free volume of the cell, or cage, N is Avogadro's number, and f a fluctuation factor which takes account of (a) the temperature variability of v, (b) the encroachment of the molecules on each other's free volume, and (c) whether or not a molecule is counted as being able to occupy the physical volume element assigned to another without exchanging places with it.

Using the ideas developed in I we proceed in this paper to investigate the liquid state. It is found that this makes possible the interpretation of the entropy rules of Barclay and Butler,[2] Bell,[3] and others,[4] and moreover makes it possible to use the information these rules contain to extend, and make more precise, our ideas regarding the molecular make-up of real liquids. The way in which one molecule interferes with the motions of another in a "normal" liquid is found to be related, in a rough, but more than qualitative way, to the heat of vaporization, and to the molal volume of the liquid. This gives a new criterion for "normal" behavior,[5] and paves the way for a realistic distinction between "normal" and "associated" liquids.

CALCULATION OF FREE VOLUME

For estimating the free volume of a liquid or solid an ingenious method due in essence to

[1] H. S. Frank, J. Chem. Phys. **13**, 478 (1945).

[2] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).

[3] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

[4] M. G. Evans and M. Polyani, Trans. Faraday Soc. **32**, 1333 (1936).

[5] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1940), 800, p. 319, discuss the commonly accepted distinction between normal and associated liquids. We shall use the words to refer to the substances to which these authors apply them, but shall find it necessary to reject their hypothesis that molecular rotations are unhindered in the liquids they consider typically normal.

Eyring[6] is available. Equation (50) of I is equivalent to writing

$$S=R\ln(\gamma V_f)+B(T), \tag{2}$$

whence

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T+P\right]=R\left(\frac{\partial \ln[\gamma V_f]}{\partial V}\right)_T. \tag{3}$$

$(\partial E/\partial V)_T$ is often used for the "internal pressure" of the liquid, and is, in all ordinary cases, far greater than P, so that, to all intents and purposes

$$\left(\frac{\partial E}{\partial V}\right)_T=RT\left(\frac{\partial \ln V_f}{\partial V}\right)_T+RT\left(\frac{\partial \ln \gamma}{\partial V}\right)_T. \tag{4}$$

Now the liquid may be thought of as subdivided into cells, of average volume V_l/N, one per molecule. The diameter of such a cell will be proportional to $(V_l/N)^{\frac{1}{3}}$, the proportionality constant depending on the assumed shape.

To describe the motion of a molecule in its cell, Eyring has used a smooth potential, hard-sphere model, and Fowler and Guggenheim,[7] following Mie,[8] have discussed a harmonic oscillator model. Neither of these is very realistic, but presumably either of them could serve as a point of departure, from which successive approximations would enable one to represent the true motion with considerable accuracy. Kincaid and Eyring[9] have made one such "improvement" on the smooth-potential model. We shall follow a more general method.

In Fig. 1, the distance l between two molecules is proportional to $(V_l/N)^{\frac{1}{3}}$, say $c(V_l/N)^{\frac{1}{3}}$. Of this, a portion $l-d$, or $c(V_l/N)^{\frac{1}{3}}-d$, is equal to the free length in which the molecule can move in the dimension considered. d is the excluded length per molecule. It is a function of temperature and volume, but corresponds to the hard-sphere diameter in the cruder model. The volume of the cell in which the molecule is free to move is then $b^3[(V_l/N)^{\frac{1}{3}}-d/c]^3$ where b^3 is a proportionality constant depending on the geometry of the packing. For a simple cubic arrangement and a cubic cell, Eyring[6] writes $b=2$, $b^3=8$. For a spherical cell, and hexagonal close packing Fowler and Guggenheim[10] write $b^3=(4/3)\pi\sqrt{2}=5.92$. We shall leave b^3 undetermined, but expect it to have a value somewhere in this neighborhood. The constant c equals 1 for simple cubic packing, and $2^{1/6}$ for hexagonal close packing. We shall write $d/c=d'$, and note that d' is strictly proportional to d and almost equal to it.

Using (1), we may now write

$$V_f=Nfb^3[(V_l/N)^{\frac{1}{3}}-d']^3=fb^3[V_l^{\frac{1}{3}}-N^{\frac{1}{3}}d']^3. \tag{5}$$

Here f is the fluctuation factor, containing both encroachment and temperature variability fluctuations. For a crystalline solid, we would expect it to have a value corresponding to $e^{\frac{1}{3}\alpha}$ as in I (54) and so to be equal to 6 or thereabouts. In a liquid the actual physical fluctuations are doubtless greater, but, on the other hand, the "looser" the relation between the molecules, the more we expect the effect of the fluctuations to be included in the "natural" size of the cell volumes, and the smaller the factor $T(\partial \ln v/\partial T)$ in f. Thus in the extreme case of the perfect gas, f as we are using it here equals 1. We shall therefore expect that in a liquid f will have a value between 1 and 5, say about 2 or 3. Its exact value will of course depend on the choice of b, but the product fb^3 could reasonably, for a liquid, be between 10 and 20.

To make use of (4) we differentiate (5) logarithmically obtaining

$$\left(\frac{\partial \ln V_f}{\partial V}\right)_T=\left(\frac{\partial \ln[b^3f]}{\partial V}\right)_T+(V_l^{\frac{1}{3}}-N^{\frac{1}{3}}d')^{-1}\times\left[V_l^{-\frac{2}{3}}-3N^{\frac{1}{3}}\left(\frac{\partial d'}{\partial V}\right)_T\right]$$
$$=f^{\frac{1}{3}}bgV_f^{-\frac{1}{3}}V_l^{-\frac{2}{3}}+\left(\frac{\partial \ln[b^3f]}{\partial V}\right)_T \tag{6}$$

where

$$g=1-3\left(\frac{N}{V_l}\right)^{\frac{1}{3}}\left(\frac{\partial d'}{\partial \ln V}\right)_T=1-\left(\frac{\partial d}{\partial l}\right)_T.$$

g measures the effect of change in volume on the exclusion diameter.

[6] H. Eyring and J. O. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).
[7] Fowler and Guggenheim, reference 5, 802, p. 325.
[8] G. Mie, Ann. d. Physik **11**, 657 (1903).
[9] J. F. Kincaid and H. Eyring, J. Chem. Phys. **5**, 587 (1937).
[10] Fowler and Guggenheim, reference 5, 806, p. 332.

With (4) this gives

$$V_f=\frac{fb^3g^3}{h^3V_l^2}\left[\frac{RT}{(\partial E/\partial V)_T}\right]^3, \qquad (7)$$

h being defined as

$$1-\frac{RT(\partial \ln [b^3f\gamma]/\partial V)_T}{(\partial E/\partial V)_T}.$$

Now Hildebrand[11] has shown that for many liquids under atmospheric pressure,

$$(\partial E/\partial V)_T=\Delta E_v/V_l,$$

where ΔE_v is the energy of vaporization of the liquid. This is true when

$$E_l=E_g-\frac{a}{V};\quad \left(\frac{\partial E}{\partial V}\right)_T=\frac{a}{V^2}=\frac{E_g-E_l}{V}. \qquad (8)$$

Even when the relation is not as simple as this, over a small volume range it must be possible to represent E_l as E_g-a'/V^n, which gives

$$\left(\frac{\partial E}{\partial V}\right)_T=\frac{na'}{V^{n+1}}=\frac{n(E_g-E_l)}{V}=\frac{n\Delta E_v}{V}. \qquad (9)$$

With (7), this gives

$$V_f=\frac{fb^3g^3}{h^3n^3}V_l\left[\frac{RT}{\Delta E_v}\right]^3. \qquad (10)$$

This is Eyring's[6] equation, "refined" by the introduction of the factors f, g, and h.

Equation (10) is now a perfectly general expression for V_f in any condensed phase. The appearance in it of the factors f, b, g, n, and h is repellent in so far as we desire a clear-cut relationship involving only experimentally measurable quantities. It would be idle, however, to try to treat a liquid as being simpler than it is, and each of the factors introduced has a physical meaning, as may be seen from the defining equations. Each of them is a property of the substance under discussion, with a definite value under given conditions of temperature and volume, and though we may not be able to estimate these values with great precision, we can tell enough about each of the quantities to be able to say, if a value is proposed, whether it is plausible or not. Actually, as will be seen, we shall use the quotient $\beta=\gamma fb^3g^3/n^3h^3$ as a property of the liquid (or solid) and shall find that its value can be calculated from experimental data. The values so obtained can, moreover, be correlated with other properties with interesting results.

[11] J. H. Hildebrand, *Solubility* (New York, 1936), second edition, p. 99.

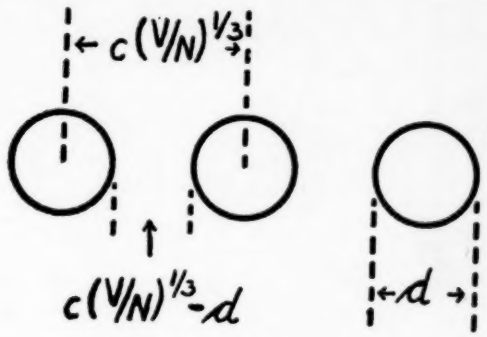

FIG. 1.

APPLICATION TO CRYSTALS

Since (10) is a general equation, it should be applicable to the elementary crystals studied in I. Comparison of (10) with I (54) should therefore give information about the factor g, since f, b, h, and n can be evaluated for those cases. For solid argon at 77.5°K, n can be evaluated from $\Delta E(=\Delta H-RT=1724$ cal./mole), V, the molal volume of the crystal ($=22.4$ cc), and $(\partial E/\partial V)_T$, obtainable from Simon and Kippert's[12] value of 38 atmos./deg. for $(\partial P/\partial T)_V$ and equal to 2945 atmos.$=71.3$ cal./cc. This makes $n=0.927$. h should be very close to 1, since $\gamma=1$ and b^3f as a quasi-geometrical quantity should not be very sensitive to volume changes. The last statement agrees with the fact that for the process of fusion, with the large expansion and the shift from solid to liquid fluctuation, ΔS is only 3.5 e.u. Again, the solid model used in

[12] F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928). Rice (J. Am. Chem. Soc. **63**, 3 (1941)) has shown that this value is too high to be reasonably accounted for by a plausible inter-atomic potential curve for solid argon, and has (J. Chem. Phys. **12**, 289 (1944)) proposed a very different sort of curve to fit this datum. We shall not enter into a discussion of the relative plausibilities of the various assumptions which may be made to resolve the difficulty, but note that a smaller value than Simon and Kippert's for $(\partial P/\partial T)_V$ of solid argon would also fit better into the picture we are presenting here, giving a smaller value for n, and therefore a smaller one for g and a larger one for $(\partial d/\partial l)_T$.

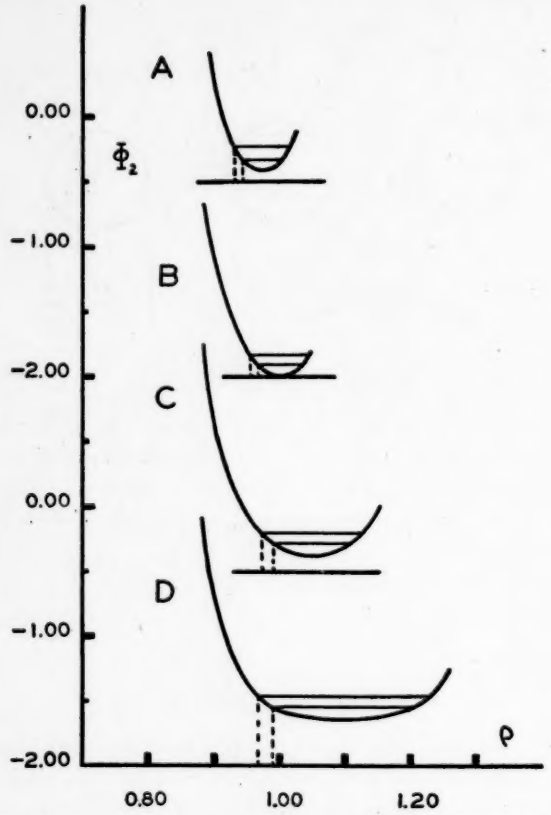

FIG. 2. $\Phi_2(=\varphi_2/D)$, the reduced potential of a molecule between two fixed neighbors, as a function of $\rho(=r/r_0)$, the reduced distance from one of them. The different curves are for different values of $\lambda(=L/r_0)$, the reduced distance apart of the "boundary" particles; for A, $\lambda=1.95$; B, $\lambda=2.00$; C, $\lambda=2.10$; D, $\lambda=2.20$. The two sets of numbers on the Φ_2 axis are for curves B and D. For A and C the ordinates $\Phi_2=-2.00$ are also shown by horizontal lines.

getting I (54) corresponds to $b=2$, $f=e^{\frac{1}{2}}\alpha=6.46$. (10) thus makes

$$\frac{V_f}{V_s}=6.46\cdot 8\cdot g^3\left[\frac{1.99\times 77.5}{1724\times 0.927}\right]^3=4.61\times 10^{-2}g^3.$$

Since the other treatment gave $V_f/V_s=5.25\times 10^{-3}$ we have $g^3=0.114$ or $g=0.48$. From the definition of g, this means that $(\partial d/\partial l)_T=0.52$. In words, this states that a small isothermal increment in V increases d by 52 percent of the increase in l. A corresponding calculation for cadmium at 523°K gives $g=0.27$ or

$$(\partial d/\partial l)_T=0.73.$$

RELATION TO POTENTIAL CURVE

The relation of the quantity $\partial d/\partial l$ to the kind of potential curve usually assumed to represent the interaction of molecules in solids or liquids is shown in Figs. 2 and 3. If the intermolecular potential for two particles is assumed[13] to be $\phi_1=ar^{-12}-br^{-6}$ where r is the distance apart of their centers, this can be thrown into the form $\phi_1/D=\rho^{-12}-2\rho^{-6}$. Here D is the "dissociation energy" of the pair, the depth of the lowest point on the curve, and $\rho=r/r_0$, where r_0 is the "equilibrium separation," or distance apart corresponding to the minimum potential. If, now, one molecule is allowed to move back and forth between two fixed molecules whose centers are separated by a distance $L=\lambda r_0$, the potential ϕ_2 of the system, ignoring the interaction of the fixed molecules with each other, is given by

$$\Phi_2=\phi_2/D=\rho^{-12}+(\lambda-\rho)^{-12}-2\rho^{-6}-2(\lambda-\rho)^{-6}.$$

This function is plotted in Fig. 2 for various values of λ in the range of interest, and shows the potential energy relationship in a simplified 1-dimensional liquid or solid. Ignoring quantum effects, the actual energy of the middle molecule will be higher than the lowest point in the curve by an amount kT. Two sets of horizontal lines

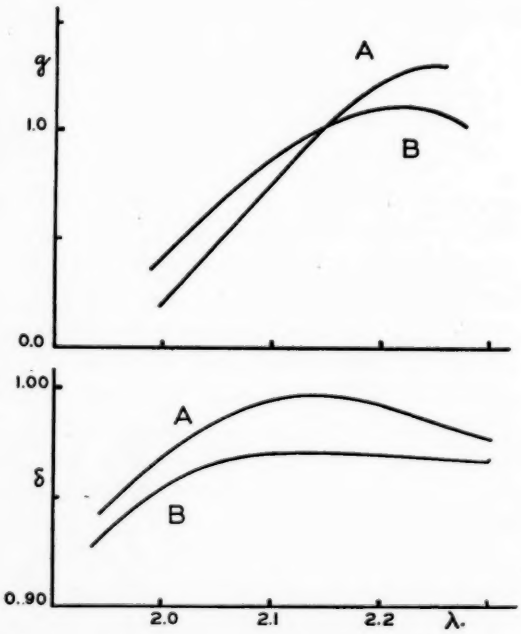

FIG. 3. $\delta(=d/r_0)$, the reduced exclusion diameter of a molecule, and $g(=1-dd/dl)$, as functions of $\lambda(=L/r_0)$ the reduced distance apart of its bounding neighbors. A, $kT/D=1/6$; B, $kT/D=1/12$.

[13] Cf., for example, J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. London **A163**, 53 (1937).

are shown in Fig. 2, representing $kT/D=\frac{1}{6}$ and $kT/D=\frac{1}{12}$, respectively. The intersections of these lines with the potential curves give the limits of the motion of the middle molecule, so that $\rho_{\text{int}}=d/r_0=\delta$. δ has been evaluated graphically, and its approximate variation with λ is shown in Fig. 3, along with $g(=1-2(\partial\delta/\partial\lambda))$. It is seen that $\partial\delta/\partial\lambda$ has rather sizable positive values when the system is highly condensed, and becomes somewhat negative when it is highly expanded. Qualitative considerations make it seem likely that this sort of trend will be found for almost any potential curve of plausible shape, and for models more realistic in detail than that considered here.

A simple generalization to three dimensions makes it possible to give a qualitative discussion of $\Delta E_v/V$, $(\partial E/\partial V)_T$ and n. We write $V=\sigma\lambda^3$ and $E=\tau D\epsilon_t$ where σ and τ are constants, and $-\epsilon_t=\phi_{2\,\min}/D-1/t$ is the distance from the zero of energy down to the line $kT/D=1/t$ before referred to. Then

$$\frac{\Delta E_v}{V}=\frac{\tau D}{\sigma}\frac{\epsilon_t}{\lambda^3}, \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_T=\frac{\tau D}{\sigma}\cdot\frac{1}{3\lambda^2}\frac{\partial\epsilon_t}{\partial\lambda}.$$

$$\frac{\epsilon_t}{\lambda^3} \quad \text{and} \quad \frac{1}{3\lambda^3}\frac{\partial\epsilon_t}{\partial\lambda}$$

are shown in Fig. 4, along with their quotient, which is n in (9) and (10). It is seen that n is less than unity for highly condensed systems and rises to values somewhat above 1 as the system is expanded. Here again, it is probable that any plausible form of potential curve and of physical model will show this qualitative behavior.

Of particular interest is the ratio g/n which occurs in (10). Figure 4 shows that for $t=6$ this ratio is near unity when n itself is near unity, and for $t=12$ the ratio is never far from 1 except when λ is very small. How much these numbers would be influenced by changes in the model or in the form of the potential curve could be determined only by a more extended study than would be appropriate here. This is also the case with the question how far the molecules of a liquid must depart from spherical symmetry before such a discussion as this becomes inapplicable. We are going to assume that for normal liquids under ordinary laboratory conditions, the

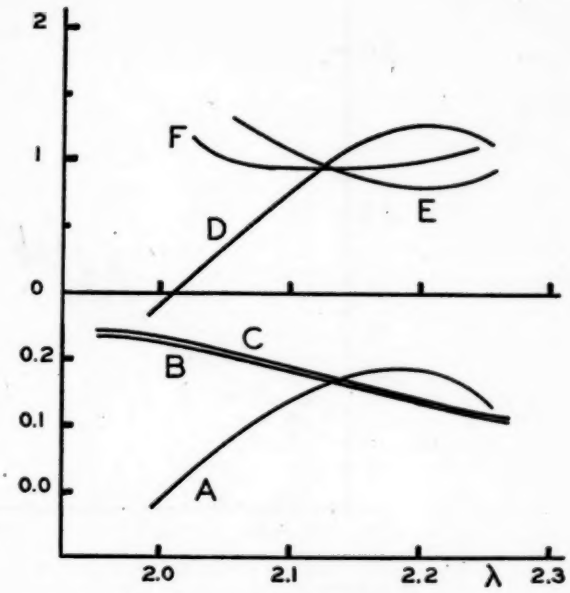

FIG. 4. Various properties of a liquid (corresponding to the simplified model described in the text) as functions of λ, which measures the degree of expansion of the liquid. Curve A represents $(1/3\lambda^2)(d\epsilon_t/d\lambda)$, which is proportional to $(\partial E/\partial V)_T$; Curves B and C represent ϵ_t/λ^3 (proportional to $\Delta E/V$), for $kT/D=1/6$ and $1/12$, respectively. Curve D represents $n(=A/B$ or $A/C)$ practically the same for either temperature. Curves E and F represent g/n for $kT/D=1/12$ and $1/6$, respectively (these correspond, respectively, to curves B and A of Fig. 3, divided by curve D.

ratio g/n has the qualitative physical meaning we have given to it, and a value which does not change much from liquid to liquid, and is not far from unity. This value is supported by the better-than-qualitative success of the calculation of compressibility made by Eyring and Hirschfelder,[6] and, as seen above, is not in conflict with the low values of g obtained here for solid (contracted) argon and cadmium. The values for cadmium correspond, of course, to averages, due to the anisotropy of the crystal.

APPLICATION TO LIQUIDS

Equation (10) gives an expression for V_f which may be introduced into the general Eqs. (50) and (51) of I. Taking the latter first and introducing (10) we get the general expression for the vapor pressure of a liquid

$$P_{\text{vap}}=\frac{RT}{\beta V_l}\left[\frac{\Delta E_v}{RT}\right]^3 e^{-\Delta H/RT}, \tag{11}$$

where

$$\beta=\gamma f b^3 g^3/h^3 n^3. \tag{12}$$

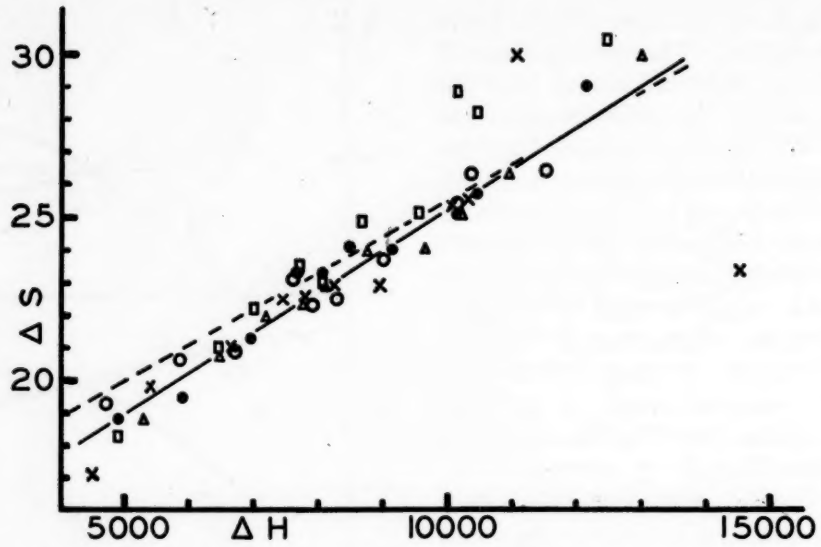

FIG. 5. ΔS of vaporization, in calories per degree per mole *vs.* ΔH of vaporization in calories per mole, at 25°C for the substances listed in Table I, which also contains the key to the symbols. The dotted line represents Eq. (16a) $\Delta S=14.5+0.0011\Delta H$. The solid line represents Eq. (17) $\Delta S=12.75+0.00124\Delta H$.

If b^3/n^3 is used instead of β (11) is identical with Eyring's[6] Eq. (17). We also follow Eyring in throwing (11) into the form

$$\frac{P_{\text{vap}}}{RT}=\frac{1}{V_{\text{vap}}}=\frac{1}{\beta V_l}\left[\frac{\Delta H}{RT}-1\right]^3 e^{-\Delta H/RT}, \quad (13)$$

and pointing out that this can be made to give the Hildebrand rule[14] for entropy of vaporization, i.e., for equilibrium vaporization to the same molal concentration of vapor all liquids should have the same molal entropy change. Eyring derives this from (13) by calling βV_l constant, remarking that most common liquids have molal volumes in the range 80–100 cc. This does not do justice to the rule, however, for it is far more accurate than such statement would imply. This may be caused in part by the fact that the function $(x-1)^3e^{-x}$ changes so rapidly with small changes of $x(=\Delta S/R=\Delta H/RT)$ in the relevant range of ΔS values ($\approx$20 e.u.), that even a considerable variation in βV_l calls for only a small change in ΔS_{vap}. We shall discuss variations in βV_l presently in another light, however, and shall find that this product may, in fact, be expected to be much the same for most liquids under the conditions envisaged in the Hildebrand rule.

[14] J. H. Hildebrand, *Solubility* (New York, 1936), second edition, p. 102.

ENTROPY OF VAPORIZATION OF LIQUIDS

Inserting (10) and (12) into (50) of I gives

$$\Delta S=R[\ln V_g-\ln(\beta V_l)+3\ln(\Delta E/RT)]$$
$$=R[\ln V_g-\ln(\beta V_l)+3\ln((\Delta H/RT)-1)]. \quad (14)$$

This tells how ΔS of vaporization of a liquid should vary with ΔH of vaporization, and gives a way of interpreting and of using the empirical rules of Bell,[3] and of Barclay and Butler,[2] which relate to these quantities. The empirical finding is that there are numerous groups of substances, pure liquids, or solutes in dilute solution, which, when compared at the same temperature and between the same standard states, give experimental values of ΔS and of ΔH which are more or less accurately represented by an equation of the form

$$\Delta S=A+B\Delta H. \quad (15)$$

A given A and B will describe a single group of substances (e.g., pure non-polar liquids, gases in benzene, aliphatic amines in water, etc.) more or less well. Moreover, Barclay and Butler[2] have shown that there is a value of A and one of B, which give a line ΔS *vs.* ΔH from which no normal substance, pure liquid nor solute, deviates very greatly. Their "normal" curve is given by

$$\Delta S=0.0277+0.0011\Delta H \quad (16)$$

TABLE I.

Substance	ΔH	ΔS	Log βV_l	V_l	Log V_l	Log β	β	$\beta/16$	HED
x 2-methyl propene	4500 LR	17.1	3.11	94.9 E	1.977	1.13	13.5	0.84	0.3
c CH_3Cl	4700 B	19.3	2.70						
d 1-butene	4900 LR	18.8	2.87	95.1 E	1.978	0.89	7.8	0.49	1.4
s trans-2 butene	4900 LR	18.3	2.98	(93.5) E	1.971	1.01	10.2	0.64	0.9
t $C(CH_3)_4$	5300 AM	18.8	2.98	122.3 E	2.087	0.89	7.8	0.49	1.4
x cis-2 butene	5400 LR	19.8	2.79	(93.5) E	1.971	0.82	6.6	0.41	1.7
c C_2H_5Cl	5870 B	20.65	2.72	72.0 LB	1.858	0.86	7.2	0.45	1.55
d 1,4-pentadiene	5900 LR	19.5	2.99	106.5 E	2.027	0.96	9.1	0.57	1.1
s $(C_2H_5)_2O$	6430 B	21.0	2.79	104.6 I	2.019	0.77	5.9	0.37	2.0
t 2-methyl 2-butene	6450 LR	20.7	2.86	106.8 E	2.028	0.83	6.8	0.425	1.7
x $Ge(CH_3)_4$	6640 K	21.0	2.83	137.7 LB	2.136	0.69	4.9	3.1	2.3
c CS_2	6680 K	20.9	2.86	60.65 I	1.783	1.08	12.0	0.75	0.55
d Si_3H_8	6950 K	21.3	2.82	132.7 LB	2.123	0.70	5.0	0.31	2.3
s $Ni(CO)_4$	7000 K	22.2	2.64	131.5 I	2.119	0.52	3.3	0.21	3.1
t $SiCl_4$	7190 K	21.9	2.74	115.4 I	2.062	0.68	4.8	0.30	2.4
x $CHCl_3$	7450 I	22.3	2.68	81.10 I	1.909	0.77	5.9	0.37	2.0
c CH_3COCH_3	7600 I	23.1	2.56	74.00 I	1.869	0.69	4.9	0.31	2.3
d Br_2	7685 K	23.3	2.54	51.5 LB	1.712	0.83	6.8	0.425	1.7
s B_5H_9	7700 K	23.5	2.49	108.9 LB	2.037	0.45	2.8	0.175	3.4
t CCl_4	7760 I	22.3	2.76	97.18 I	1.988	0.77	5.9	0.37	2.0
x PCl_3	7780 K	22.5	2.71	87.65 I	1.943	0.77	5.9	0.37	2.0
c CSeS	7900 K	22.3	2.78	62.3 LB	1.794	0.99	9.8	0.61	1.0
d CH_3OH	8040 B	23.3	2.58	40.72 I	1.610	0.97	9.3	0.58	1.1
s C_6H_6	8050 B	23.0	2.67	89.50 I	1.952	0.72	5.25	0.33	2.2
t $GeCl_4$	8090 K	22.9	2.69	114.5 LB	2.019	0.67	4.7	0.29	2.7
x PBr_3	8230 K	22.9	2.72	95.5 LB	1.980	0.74	5.5	0.34	2.1
c 2,2,4-trimethyl pentane	8275 P	22.5	2.81	166.1 E	2.220	0.59	3.9	0.24	2.8
d Cl_2O_7	8480 K	24.1	2.49						
s $CH_3COOC_2H_5$	8670 B	24.9	2.34	98.50 I	1.993	0.35	2.2	0.14	3.9
t n-heptane	8740 P	23.9	2.58	147.4 E	2.168	0.41	2.6	0.16	3.6
x $Zn(C_2H_5)_2$	8960 K	22.9	2.83	105.3 LB	2.022	0.81	6.5	0.41	1.8
c 2,3,4-trimethyl pentane	9000 P	23.7	2.66	161.9 E	2.209	0.45	2.8	0.175	3.4
d Toluene	9115 PS	24.0	2.62	107.0 I	2.029	0.59	3.9	0.24	2.8
s $SnCl_4$	9550 K	25.1	2.44	117.8 I	2.071	0.37	2.3	0.14	3.8
t $TiCl_4$	9620 K	24.0	2.69	110.6 I	2.044	0.65	4.5	0.28	2.5
x $C_2H_4Br_2$	10050 RA, I	25.3	2.47	86.60 I	1.937	0.53	3.4	0.21	3.1
c C_6H_5Cl	10110 ZS, I	25.4	2.46	102.1 I	2.009	0.45	2.8	0.175	3.4
d p-xylene	10110 PS	25.1	2.52	123.9 LB	2.093	0.43	2.7	0.17	3.5
s C_2H_5OH	10120 B	28.9	1.70	58.65 I	1.768	−0.07	0.85	0.053	5.8
t m-xylene	10160 PS	25.1	2.53	123.6 LB	2.092	0.44	2.8	0.175	3.5
x S_2Cl_2	10300 K	25.7	2.41	81.10 I	1.909	0.50	3.2	0.20	3.2
c 1-$C_3H_7NO_2$	10380 H	26.3	2.30	89.9 LB	1.954	0.35	2.2	0.14	3.9
d o-xylene	10470 PS	25.7	2.43	123.6 LB	2.092	0.34	2.2	0.14	3.9
s H_2O	10470 I	28.22	1.88	18.07 I	1.257	0.62	4.2	0.26	2.7
t mesitylene	10930 B	26.3	2.36	140.0 LB	2.146	0.21	1.6	0.10	4.5
x n-C_3H_7OH	11050 B	29.9	1.60	75.05 I	1.875	−0.28	0.52	0.032	6.8
c $GeBr_4$	11510 K	26.4	2.42	126.0 LB	2.100	0.32	2.1	0.13	4.0
d H_2O_2	12130 K	29.0	1.92	23.69 I	1.374	0.55	3.55	0.22	3.0
s n-$C_5H_{11}OH$	12450 B	30.4	1.66	108.8 LB	2.037	−0.38	0.42	0.026	7.2
t n-$C_6H_{13}OH$	13050 B	29.90	1.82	128.2 LB	2.108	−0.29	0.51	0.032	6.8
x Hg	14540 K	23.30	3.40	14.84 I	1.171	2.23	170.0	10.6	−4.7
c Cs	18340 K	30.0	4.34	72.2 I	1.858	2.48	304.0	18.9	−5.85

The letters *x*, *c*, *d*, *s*, *t*, refer, respectively, to the symbols, cross, circle, dot (filled circle), square, and triangle, by which the substances so denoted are plotted in Figs. 5–9.

AM = J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).
B = I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).
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LR = A. B. Lamb and E. E. Roper, J. Am. Chem. Soc. **62**, 806 (1940).
P = K. S. Pitzer, J. Am. Chem. Soc. **62**, 1227 (1940); **63**, 2413 (1941).
PS = K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. **65**, 803 (1943).
RA = D. Radulescu and M. Alexa, Chem. Abs. **34**, 934 (1940).
ZS = A. A. Zil'bermann-Granovskaya and E. A. Shugam, J. Phys. Chem., USSR **14**, 1004 (1940).

Note.—Where ΔH values had to be obtained by the application of the Clausius-Clapeyron equation, estimated corrections were applied to account for gas imperfection.

in their units, which are kg. cal./deg./mole for ΔS, and kg. cal./mole for ΔH. They take for the standard state of the gas a partial pressure of 1 mm of mercury at 25°C, and for the liquid, the

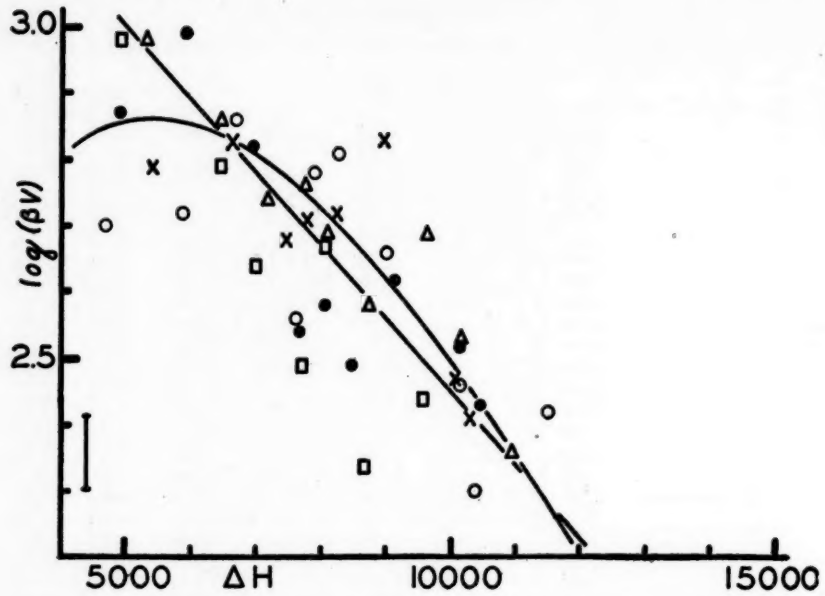

FIG. 6. $\text{Log}_{10}(\beta V_l)$ *vs.* ΔH of vaporization in calories per mole for the liquids of Table I. The curved line represents Eq. (18) $\log(\beta V_l) = 1.600 - 0.0002712\Delta H + 3\log(\Delta H/RT - 1)$. The straight line represents Eq. (19) $\log(\beta V_l) = 3.55 - 0.00011\Delta H$. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calories per degree per mole in entropy.

pure liquid, at 25°C. We prefer to use different units, calories per degree per mole, and calories per mole, for ΔS and ΔH. We also prefer to use 1 atmosphere at 25°C as the standard state for the gas, but shall keep their standard state for liquids. In these units, and between our standard states, then, (16) becomes

$$\begin{aligned}\Delta S &= 27.7 - R\ln 760 + 0.0011\,\Delta H \\ &= 27.7 - 13.2 + 0.0011\,\Delta H \\ &= 14.5 + 0.0011\,\Delta H. \qquad (16a)\end{aligned}$$

An alternative line, which seem slightly better, is given by

$$\Delta S = 12.75 + 0.00124\,\Delta H. \qquad (17)$$

In Fig. 5 (16a) is plotted as the dotted line, and (17) as the solid one. The experimental points are for the substances presented in Table I. Some of the data are those used by Barclay and Butler, and some are from other sources, as noted.

The reality of the rule depends both on the accuracy of the data and on whether enough liquids of enough different kinds have been used to insure against a "proof by selection." As to the first point, Table I shows, in fact, that ΔH and ΔS values calculated from *International Critical Tables* data, or from more recent sources, often disagree with those given by Barclay and Butler. The disagreements, however, are not such as to weaken the support given to the rule. As for the generality of the relationship as a rule for unassociated liquids, this is strongly supported by the points for inorganic liquids. The experimental uncertainty in the ΔS values may, in unfavorable cases, exceed 0.5 e.u., and to this order of accuracy the constants of (16a) represent the data fairly well. It seems, however, that a slightly better representation of the less polar liquids is given by (17).

There is under way in this laboratory a more extensive examination of data which have been critically chosen, and to which corrections for gas imperfection have been applied in evaluating ΔH and ΔS. The results will be communicated in a separate publication. Several points may be mentioned here, however. First, the gas imperfection corrections may be important, and if detailed theoretical questions are to be discussed, corrected values should be considered. Second, the conjecture of Barclay and Butler that different groups of substances might be representable with high precision by separate straight lines which differed somewhat from

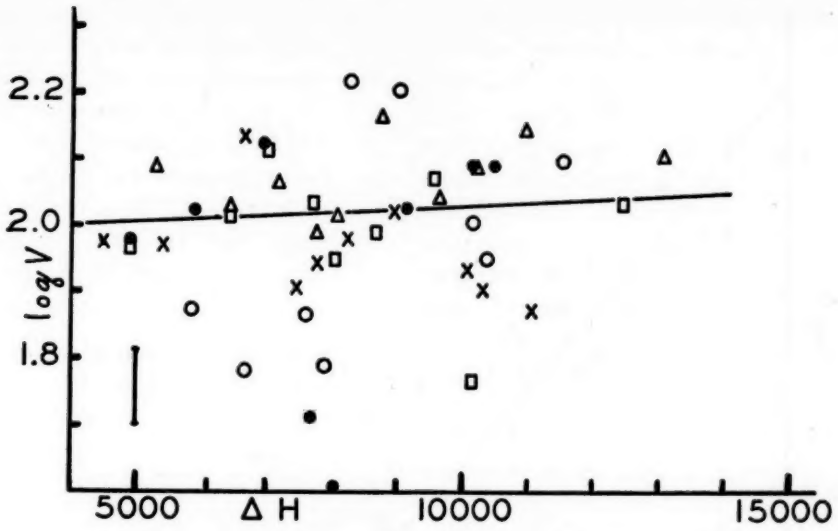

FIG. 7. $\text{Log}_{10}\, V$ *vs.* ΔH of vaporization in calories per mole, for the liquids of Table I. The line represents Eq. (20) $\log V = 1.98 + 0.000005\Delta H$. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calories per degree per mole in entropy.

group to group is confirmed in several cases. Third, the differences between these group lines seem, in some cases at least, to be related to the structural features of the molecules in a way which is intelligible in terms of the discussion of the next few paragraphs.

A ROUGH NUMERICAL RULE FOR β

It is clear that (17) does represent a sort of normal behavior, and comparison with (14) shows that this is equivalent to an assertion that $\ln(\beta V_l)$ must, in a general sort of way, be a function of ΔH. Combining (14) and (17) one obtains, after a little arithmetic,

$$\log_{10}(\beta V_l) = 1.600 - 0.000271\Delta H + 3\log_{10}\left(\frac{\Delta H}{RT} - 1\right). \quad (18)$$

(18) is plotted in Fig. 6, along with values of $\log(\beta V_l)$ for the substances of Table I, computed from (14) and the experimental ΔS and ΔH values. It is seen that in the range $\Delta H = 6{,}000$–12,000 cal./mole both (18) and the experimental points for normal liquids show something like a linear decrease in $\log(\beta V_l)$ as ΔH increases. One infers that there is some sort of general influence at work here, modified in each substance by more or less pronounced specific effects. The strongly curved portion of (18) (ΔH below 6000–7000 cal./mole) falls among the liquids whose 25° vapor pressures are so high that gas imperfections become considerable. These cases present no difficulty in principle, and it may be that a future study of substances falling in this region will yield interesting results. For the present, however, we limit our discussion of pure liquids, both from the standpoint of (18) and of (17), to cases in which ΔH exceeds 5 or 6 kg cal./mole. In this range (18) can be approximated very well by the linear equation

$$\log(\beta V_l) = 3.55 - 0.00011\,\Delta H. \quad (19)$$

The spread of the experimental points about the line (19) in Fig. 6 is considerably greater than the spread about (17) in Fig. 5. This is only partly due to the scale of plotting, as shown by comparison with the vertical line drawn in Fig. 6, which corresponds to an entropy discrepancy of 0.5 e.u. The reason is doubtless that there is some compensation between ΔH and ΔS, as discussed below, so that either experimental error or anomalous behavior will be accentuated in $\log(\beta V_l)$, which involves a difference between quantities which depend on ΔH and ΔS, respectively. Comparison of the discrepancies from (19) with those from (17) indicate that many of them, at least, represent real physical effects,

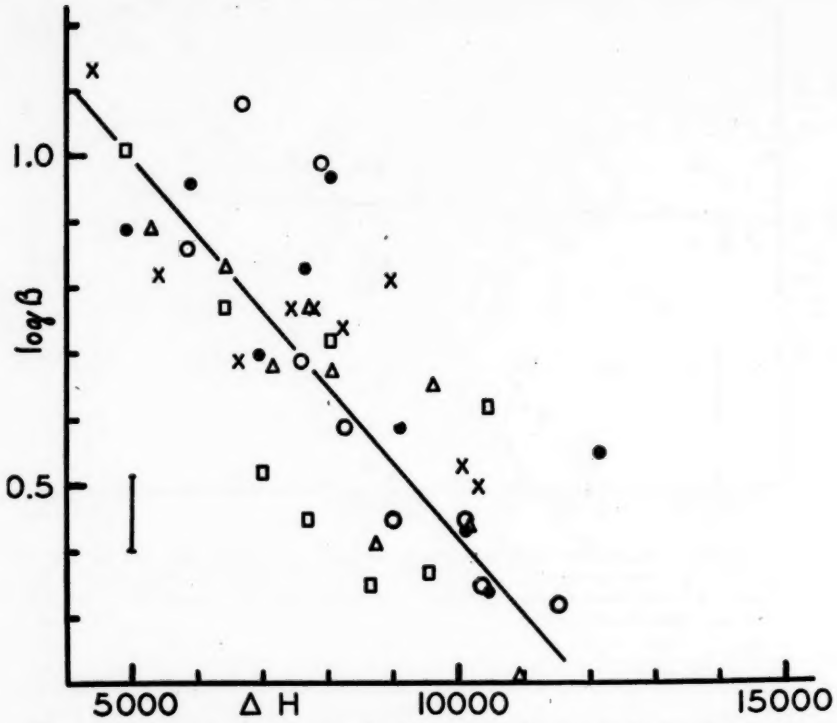

FIG. 8. $\text{Log}_{10}\beta$ *vs.* ΔH of vaporization in calories per mole for the liquids of Table I. The line represents Eq. (21) $\log\beta = 1.57 - 0.000115\Delta H$. The vertical line has a length of 0.114 units in the logarithm, corresponding to a range of 0.5 calorie per degree per mole in entropy.

which are therefore specific, over and above the general rules represented by (17) and (19).

Since specific effects enter as largely as they do, there would be no utility, at this stage, in a discussion of hypothetical exact functional relationships to which (17), (18), and (19) approximate. It is enough for the present to have discovered so good a linear trend in $\log(\beta V_1)$ with ΔH as the Barclay-Butler rule has been shown to imply, and to inquire into its qualitative physical significance.

For this purpose we must first separate out the dependence, if any, of $\log V$ upon ΔH. In Fig. 7, these quantities are plotted for the liquids of Table I, and it would be rash to claim that any marked dependence stands out. The ordinary expectation would be that $\log V_l$ should, in a general sort of way, increase with ΔH, from the Trouton rule and the idea that variations in density within a group of liquids are not extreme. It is clear, however, that for this miscellaneous series of liquids, specific, or constitutive, effects are so great as to mask any obvious emergence of such a rule.

The equation

$$\log V_l = 1.98 + 0.000005\,\Delta H \qquad (20)$$

is derived from (21) and (19), and is plotted as the solid line in Fig. 7. While it would seem foolish to say that it describes a "normal trend" in the experimental points, closer examination suggests that it may not be devoid of significance. Substances which lie very much below, or to the right of (20) are, in striking majority, polar. That is, they have forces acting between the molecules which are absent in the non-polar liquids and which may pull the liquid together "too much," or may raise ΔH to values higher than their volumes (number of electrons which can participate in van der Waals interaction) correspond to. Substances which lie very much above, or to the left of (20) have "balled-up" molecules, or electron distributions which separate the electrons of neighboring molecules "too far," so that the van der Waals attraction is below par, ΔH is too small, and the liquid is "abnormally" expanded.

The points for H_2O and H_2O_2, and the normal

aliphatic alcohols, are in agreement with this picture. In the cases of the metals Hg and Cs, the forces holding the liquid together are different in kind (cf. discussion below).

When the individual values of $\log V_l$ are used to obtain $\log \beta$, results are obtained which are plotted against ΔH in Fig. 8. Here a rather good linear trend reappears and Eq. (21) represents the line which has been chosen to express it.

$$\log \beta = 1.57 - 0.000115\, \Delta H. \qquad (21)$$

Examination of the deviations of the individual points from (21), and comparison with them of the deviations of points for $\log (\beta V_l)$ from (19), indicates a correlation which seems more than random. This lends some additional support to the idea that (20), and deviations from it, can be interpreted in a physically significant way. A closer analysis of these questions belongs to a more detailed study than is attempted here. As to order of magnitude, however, the liquids for which ΔH is greater than 6000 cal./mole, excluding the hydrogen bonded substances and the metals, show average deviations from (19), (20), and (21) of just under 0.10 in the logarithm in each case. These correspond to deviations of about 0.4 e.u., or in (19) and (21) to deviations of 800 cal./mole in ΔH. The existence of such large deviations is undoubtedly due in part to the attempt to fit so miscellaneous a group of liquids with a single representation.

PHYSICAL INTERPRETATION

To interpret (21) in terms of the physical picture, we recall that $\beta = (\gamma f b^3 g^3 / h^3 n^3)$. The product fb^3 may change somewhat from liquid to liquid, but we do not expect the change to be great. g/n, as we have seen, should be close to 1 for all ordinary liquids but small variations in this ratio should show up as specific effects in β. h should be close to 1 when $\gamma = 1$, and will be somewhat less than 1 otherwise, as γ should increase with V, though perhaps not greatly. The chief burden of a general variation in β with ΔH therefore falls on γ, and (21) thus shows that γ decreases with increase in ΔH. This, again, is qualitatively what is to be expected for the kinds of molecules that make up real liquids. The larger the molecules, the greater, normally, will be the van der Waals attraction between them, and the greater, therefore, the repulsive forces between them for equilibrium. This means more intimate contact, and therefore, for polyatomic molecules, more interference with internal motions—chiefly rotation and internal rotation. It is striking that, for a series of hypothetical monatomic liquids with ΔH in the range of interest, calculations from Pitzer's[15] reduced equation of state data indicate that β would be practically independent of ΔH, and have the high value of about 16. For these liquids $\gamma = 1$ identically, and it appears that 16 is a sort of normal or "unperturbed" value for β for any non-metallic liquid. This would mean that except for peculiarities in f, b^3, or g/n the factor by which β is less than 16 measures the extent to which the internal motions are interfered with when the vapor condenses. As pointed out above, this is qualitatively reasonable as an explanation of (21), and the discussion following (5) shows that 16 is a very reasonable par value for β to have.

SOME ABNORMALITIES

The β values for several abnormal liquids stand out prominently as exceptions to what has just been said. In the case of mercury, $\beta = 170$, the explanation is undoubtedly to be found in the fact that the forces between the atoms are of a different sort from those existing in non-

[15] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).

Pitzer tabulates $\phi_l (= V_l/V_c)$, $\log \pi (\pi = P_{vap}/P_c)$, V_g/V_l, and ΔS_{vap}, for variable values of $\vartheta (= T/T_c)$ for the ideal liquid in equilibrium with its saturated vapor. Corrections can be made for gas imperfection using the Berthelot equation. Then ΔS_{vap} yields V_g/V_f, which, with the tabulated V_g/V_l gives V_f/V_l. Since this ΔS is an equilibrium quantity $\Delta S/R = \Delta H/RT$, so that β is easily obtained. It is noteworthy that ΔH_{vap} contains T_c as a factor, and, if T is to be 25°C, T_c cannot be higher than about 533°K without making ϑ so low (<0.56) that the ideal liquid would freeze. On the other hand, this makes ΔH only some 5600 cal./mole.

The fact that $\Delta H = 5600$ is the highest value for which β can be calculated for an ideal liquid at 25°C detracts somewhat from the comparison here made. The meaning of the calculation, however, is that β is sensibly independent of temperature for these liquids, which justifies using the value 16.0 as a "norm" for any liquid at any temperature.

Incidentally, it appears that most ordinary liquids, with $\Delta H \geqslant 6000$ cal./mole, would be solids at room temperature if they behaved as ideal substances. The reason that they are liquids at room temperature, then, is that in melting they gain entropy from sources which are not available to the ideal liquid—orientations and bendings. It is very striking that hexamethyl ethane, which is so bunched up and symmetrical as to be of nearly "ideal" shape, melts at about 102°C (G. Egloff, *The Physical Constants of Hydrocarbons* (Reinhold Publishing Corporation, New York, 1939), p. 57), compared with melting points well below 0°C for all the other open chain hydrocarbons of C_8 or below. The high melting points of benzene and cyclohexane also support this point of view.

metallic liquids.[15] This results in the higher degree of condensation of the liquid (small molal volume), which is reflected in the low value of $n(=0.33^{11})$. It may also change f, b, and g/n to values different from those found in non-metallic liquids. Taking $\gamma=1$, and putting the whole burden of the anomaly on g/n, we get $(g/n)^3=170/16=10.7$. This makes $g/n=2.2$, approximately, a value not incompatible with the qualitative results of Fig. 4.

In the case of methyl alcohol, $\beta=9.3$, approximately, about twice the normal value for $\Delta H=8040$. Here, however, we know that n is again about 0.33^{11}. This might well lead to a value of $(g/n)^3$ somewhere about 10, so that if γ were equal to 1 we would expect β to be about as far from the normal curve as in the case of mercury. The conclusion is that γ is very much less than unity in this case, in excellent agreement with what we know about hydrogen bonding in the alcohols.

For ethyl alcohol $n\approx\frac{1}{2}$. This should cause a reduction in $(g/n)^3$ as compared with methyl alcohol. This should hardly cause a so pronounced decrease in β as is observed, however, the value here being about 0.85 (the increase of about 2000 calories in ΔH should normally reduce β by about 60 percent). A plausible explanation is that the longer C_2H_5OH molecules are relatively more hindered in their rotations by hydrogen bonding than are the CH_3OH molecules, so that β is smaller here.

As mentioned later, the alcohols provide cases where the free-volume concept is less clear-cut than we could wish, and it seems scarcely worth while to pursue the details of their behavior further. Empirically, it appears that the effect of the OH group becomes relatively less and less important as the hydrocarbon chain is lengthened, so that n-hexyl alcohol behaves very much like a hydrocarbon with the corresponding ΔH of vaporization.

CS_2 and CSeS seem also to have β values which are higher than might be expected, particularly in view of their straight-line structure, which should cause marked interference with free rotation in the liquids. Their small molal volumes suggest that here again we have liquids which are more "condensed" than normal, and that the high β is due to large g/n. Hildebrand's figure 0.89 for n for CS_2 can be taken as being in harmony with this conjecture. Hildebrand's value of $n=1.21$ for $TiCl_4$ is in the opposite direction, however, in relation to the large value of β for this compound, and the tetrahalides of C, Si, Ge, Ti, and Sn will presumably require special discussion. The large β for $Zn(C_2H_5)_2$ may also reflect some difference in force field as compared with the "standard."

THE BARCLAY-BUTLER RULE

The physical meaning of the Barclay-Butler rule may now be stated in words. When a vapor condenses, a molecule, so to speak, falls into a potential well. The deeper this well, i.e., the greater the loss of energy on condensation, the narrower it is, and the smaller the free volume, therefore the greater the loss in entropy. In addition, the deeper and narrower the well the greater the interference tends to be, not only with moving back and forth, but also with squirming into different positions. This also means more loss of entropy in deeper wells. The fact that the resultant dependence of ΔS on ΔH turns out to be approximately linear, may or may not be significant—this is a point which it does not seem profitable to discuss further at this time. The fact that individual substances show specific deviations from the Barclay-Butler line is not surprising, since there are so many factors which might cause such deviation. The fact that there are so many substances of such diverse types for which the deviations are comparatively small seems to justify setting up an equation like (17) as a rough definition of normal behavior. It is to be noted that this sort of normality does not mean correspondence with such a reduced equation of state as Pitzer's[15] for an "ideal" substance, nor with the model described by Fowler and Guggenheim,[5] but rather with the normal, i.e., usual, tendency which real polyatomic substances have to depart from these.

THE HILDEBRAND RULE

Since a small value of β usually means a small γ, which means that the free rotation of a vapor molecule has been replaced by a librational motion in the liquid, small β should mean large negative ΔC_P of vaporization. This agrees with the correlation found by Pitzer[15] between ΔS and ΔC_P of vaporization for substances deviating from his figures for ideal liquids.

This correlation also enables us to add another

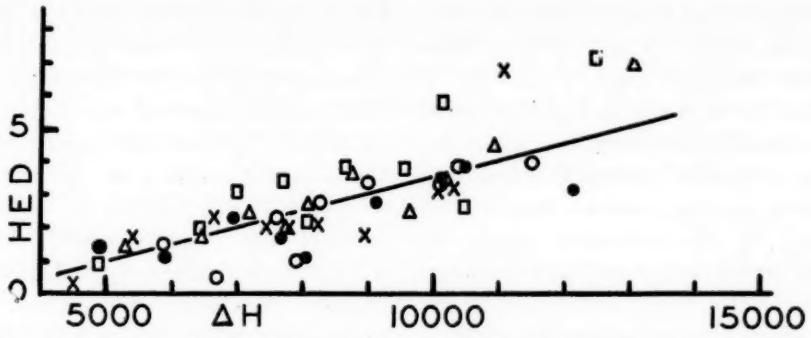

FIG. 9. The hypothetical entropy defect in calories per degree per mole *vs.* ΔH of vaporization in calories per mole, for the liquids of Table I. The line represents Eq. (23) $\text{HED} = -1.70 + 0.00053\Delta H$.

point to the discussion of the Hildebrand rule. Our rule (21) for variation of β from substance to substance was derived from measurements all at one temperature, in this case 25°C. The product βV_l in Hildebrand's rule (13), however, is to be taken at a different temperature for each substance, and since it is the constancy of $\Delta H/T$ that is under discussion, it follows that the greater ΔH for a given substance, the higher the temperature at which βV_l must be taken. Since ΔC_P values more negative than -7 cal./deg./mole correspond to an increase in βV_l with temperature,[16] and since the real liquids under consideration have $-\Delta C_P$ values of about 10, we have the following kind of compensation:[17] the greater ΔH of vaporization (and ΔH is in general so great that there is no qualitative difference between the values at 25°C and at the Hildebrand temperature) the lower βV_l at 25°C, but the greater the upward correction to be made to it in going to the Hildebrand temperature. Qualitatively, therefore, it is not surprising that βV_l has similar values for all normal liquids at the Hildebrand temperatures.

THE HYPOTHETICAL ENTROPY DEFECT

The qualitative success of the Trouton rule is due to the fact that boiling liquids are, roughly, in corresponding states. Hildebrand's rule is an improvement on Trouton's because[14] it compares liquids in states which "correspond" more accurately than do the normal boiling points. According to Pitzer,[15] a further theoretical improvement could be made by comparing liquids at equal liquid to vapor volume ratios instead of at equal molal concentrations of vapor. Now the fact that β can be calculated unambiguously as a function of ϑ for an ideal liquid means that β is a *reduced quantity*. Furthermore, the empirical fact that β has a constant value, independent of ϑ, for Pitzer's ideal liquid, seems suggestive. We are going to propose, as a tentative hypothesis, that β is strictly invariant for the perfect liquid. If this is true, then comparison of β values for real liquids is logically equivalent to the comparison of ΔS under corresponding conditions, and the departure of β from the value 16.0 found for the ideal liquid is a measure of the departure of the real liquid from ideality. We therefore define

$$\text{HED} = R \ln \left(\frac{16.0}{\beta}\right) \qquad (22)$$

as the *hypothetical entropy defect* of a real liquid. By our hypothesis this is the amount by which the entropy of the real liquid is less (compared with its vapor as an ideal gas in some standard state) than that of an ideal liquid would be under corresponding conditions. HED values (for 25°C) are listed in Table I and plotted in Fig. 9. (21) requires that, as a rough empirical rule,

$$\text{HED} = -1.70 + 0.00053\,\Delta H \qquad (23)$$

give a line which shall represent the 25°C values

[16] Without entering here into a full discussion of the variation of β with T in real liquids, we may remark that (14) leads to the relation

$$\frac{\partial \ln \beta}{\partial \ln T} = 1 - \frac{\partial \ln V_l}{\partial \ln T} - 3\left(1 - \frac{RT}{\Delta H}\right)^{-1} - \frac{\Delta C_P}{R}\left(1 - \frac{4RT}{\Delta H}\right)\left(1 - \frac{RT}{\Delta H}\right)^{-1}.$$

This shows that the more negative ΔC_P, the more strongly β increases with T in qualitative agreement with our physical picture. Numerically $\partial \ln \beta / \partial \ln T$ at 25°C is predicted to be positive for ΔC_P more negative than about -7.0 at $\Delta H = 7200$, or about -6.0 at $\Delta H = 10{,}800$.

[17] Cf. note at end of reference 2.

for the normal liquids here treated with an average discrepancy of about 0.5 e.u. This is illustrated in Fig. 9 by the solid line.

What is said above shows that a good part of the HED of a normal liquid must be caused by the fact that the molecular rotation is less free in the liquid than in the gaseous state. This relates the HED to the discussion given by Hildebrand[18] of liquid structure and entropy of vaporization, with this difference, that Hildebrand, in effect, is comparing βV_l values at the Hildebrand temperature rather than β values at 25°C. The discussion by Halford[19] of the connection between ΔS and the length of free swing required for rotational motion in a liquid is also closely related to the present treatment.

As implied by the remarks made above on CS_2, CSeS, etc., however, the HED is not restricted to effects of hindered rotation, for the derivation of (14) is general enough to free (22) from the limitations of the approximate rules (17)–(21). We have seen that differences from a "normal" potential function must affect β through g and n. Differences from normal packing and dynamical behavior will be accounted for through b, f, g, h, and n. So long, therefore, as the general conditions for the physical meaningfulness of the free volume representation are fulfilled, and in so far as the concept of corresponding states is useful, the deviation of β from 16.0 should be able to express the entropy anomaly of any real liquid, arising from any cause or combination of causes. It should then be both useful and correct to use the large negative HED of mercury, for example, to express the fact that this liquid has a molal entropy considerably larger than an ideal, and very much larger than an "ordinary" liquid would have under corresponding conditions.

SIZE OF FREE VOLUME

We conclude the discussion of pure normal liquids by calculating the numerical values of V_f and V_f/V_l in sample "standard" cases. From (2)

$$\Delta S = 4.575(\log V_g - \log(\gamma V_f)),$$

or, with $V_g = 24{,}400$ cc,

$$\log \gamma V_f = 4.389 - \frac{\Delta S}{4.575}. \qquad (24)$$

For a liquid of $\Delta H = 7000$ cal./mole, (17) gives $\Delta S = 21.4$ e.u. so that $\gamma V_f = 0.512$ cc. We can estimate γ as $\beta/16 = 0.36$ taking β from (21). This makes $V_f = 1.42$ cc. Taking V_l from (20) as 102 cc, $V_f/V_l = 0.014$ approximately. Making the same calculation for $\Delta H = 10{,}000$ cal./mole, $\gamma V_f = 0.078$ cc, $\gamma = 0.165$, $V_f = 0.47$ cc, $V_l = 107$ cc, so that there $V_f/F_l = 0.0044$. These values for V_f/V_l, while rather artificial, show the expected relation to the V_f/V_s values found in I for monatomic solids, which were about $\frac{1}{2}$ percent. Our V_f's for liquids are by definition larger by the factor $16.0/\beta$ than the values obtained from vapor pressures by Kincaid and Eyring,[20] who also, in effect, took $\beta = 8$. This factor disturbs the otherwise almost exact agreement they found between "vapor-pressure" and "sound-velocity" values of V_f. It seems, however, that a factor of 2 is not too great a discrepancy to expect between V_f as defined here and that obtained by the sound-velocity method.

ASSOCIATED LIQUIDS

In view of the wide, and well-known, deviations of "associated" liquids from such rules as those of Trouton or Hildebrand and of Ramsay and Shields, it seems at first rather remarkable that the points for the alcohols, for the amines, and particularly for water, fall as close as they do to the Barclay-Butler line for pure liquids (cf. Fig. 5 where the "excess" ΔS for these substances is seen to be about 2 e.u. as compared with 5 or 6 e.u. discrepancies from the other rules. 2.2 e.u. is about $R \ln 3$). The explanation of course is in part that different factors tend to compensate each other, as found above with γ and $(g/n)^3$ and, to some extent, with β and V_l. Another compensation comes about in that the heats and entropies of vaporization of these liquids turn out to be about "equally abnormal." The hydrogen bond, or surface dipole, interactions between the molecules act to increase both the energy of separation and the restriction of motion beyond what is typical for liquids which are non-polar or have "buried" dipoles. It appears that the relation between the extra ΔH contribution and extra ΔS contribution due to "association" is not very different from the "normal" relation between

[18] J. H. Hildebrand, J. Chem. Phys. **7**, 233 (1939).
[19] R. S. Halford, J. Chem. Phys. **8**, 496 (1940).
[20] J. F. Kincaid and H. Eyring, J. Chem. Phys. **6**, 620 (1938).

ΔH and ΔS, so that instead of falling far away from the Barclay-Butler line they fall somewhere near it, but in the "wrong" places—i.e., in a range of ΔH and ΔS values higher than their molecular weights and molecular volumes would normally correspond to.

Another point which needs to be mentioned here is that these substances constitute the cases in which the free volume picture is least clear-cut. The occurrence of hydrogen bonds in these liquids introduces a specific non-classical element into the motions (both translational and rotational) of the molecules in the liquid state. On the other hand, by using a sort of principle of correspondence, we can see that, however bad the focus, the free volume camera we have used to make pictures of the simpler liquids must also give some sort of picture for these. And until some better basis is devised for comparing the associated liquids with the non-associated it seems probable that the free volume concept will continue to be useful for this purpose.

SOLUTIONS

The interpretation of liquids which has been given above receives further, and not inconsiderable, support from data on solutions. It also permits interesting conclusions to be drawn from solution data. The necessary extension of the theory, together with an analysis of experimental results, will be found in the following paper, No. III of this series.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 11 NOVEMBER, 1945

Free Volume and Entropy in Condensed Systems

III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes

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(Received June 4, 1945)

The ideas of the first and second papers in this series, which make it possible to interpret entropy data in terms of a physical picture, are applied to binary solutions, and equations are derived relating energy and volume changes when a solution is formed to the entropy change for the process. These equations are tested against data obtained by various authors on mixtures of normal liquids, and on solutions of non-polar gases in normal solvents. Good general agreement is found, and it is concluded that in such solutions the physical picture of molecules moving in a "normal" manner in each others' force fields is adequate. As would be expected, permanent gases, when dissolved in normal liquids, loosen the forces on neighboring solvent molecules producing a solvent reaction which increases the partial molal entropy of the solute. Entropies of vaporization from aqueous solutions diverge strikingly from the normal behavior established for non-aqueous solutions. The nature of the deviations found for non-polar solutes in water, together with the large effect of temperature upon them, leads to the idea that the water forms frozen patches or microscopic icebergs around such solute molecules, the extent of the iceberg increasing with the size of the solute molecule. Such icebergs are apparently formed also about the non-polar parts of the molecules of polar substances such as alcohols and amines dissolved in water, in agreement with Butler's observation that the increasing insolubility of large non-polar molecules is an entropy effect. The entropies of hydration of ions are discussed from the same point of view, and the conclusion is reached that ions, to an extent which depends on their sizes and charges, may cause a breaking down of water structure as well as a freezing or saturation of the water nearest them. Various phenomena recorded in the literature are interpreted in these terms. The influence of temperature on certain salting-out coefficients is interpreted in terms of entropy changes. It appears that the salting-out phenomenon is at least partly a structural effect. It is suggested that structural influences modify the distribution of ions in an electrolyte solution, and reasons are given for postulating the existence of a super-lattice structure in solutions of $LaCl_3$ and of $EuCl_3$. An example is given of a possible additional influence of structural factors upon reacting tendencies in aqueous solutions.

INTRODUCTION

IN the first of two preceding papers[1] (hereinafter to be referred to as I and II) the concept of free volume was re-examined, and relations were worked out between free volume changes and changes in entropy in isothermal processes. In the second paper these free volume relation-

[1] H. S. Frank, J. Chem. Phys. **13**, 478, 493 (1945).

ships were used to derive an equation connecting ΔS with ΔH for the process of vaporization of a liquid. This equation was compared with the empirical rule of Barclay and Butler,[2] and it was found that the comparison provided an instructive interpretation of the physical details of the condensation, or vaporization, process.

Free volume treatments of liquids have been extended to binary mixtures before,[3] but never, to our knowledge, from the empirical point of view of the present series of papers. In this third paper the method of the first two is generalized to binary systems, and it is shown that the simplest sort of generalization suffices to bring the empirical rules of Bell[4] and of Barclay and Butler[2] for solutions of "normal" substances within the framework set up for the interpretation of pure liquids. In addition, it is found that the "anomalous" entropy of formation found by Scatchard, Lacher, and their coworkers[5] for mixtures of various pairs of liquids bears a relationship to the heat of mixing which is predictable by this theory.

The establishment of a plausible physical interpretation of partial molal entropies in solutions of normal substances furnishes the necessary background for the discussion of the very abnormal case of aqueous solutions. It is found that the peculiar nature of water plays a very important role in determining the solubility behavior in it both of non-polar and of ionic substances, and the numerical values of entropy of hydration both for non-polar and for ionic solutes are used to draw pictorial conclusions regarding their effect on the water structure. In the latter case, the conclusions reached are supported by data from many other fields, and suggest interesting possibilities for electrolyte theory.

[2] I. M. Barclay and J. A. V. Butler, Trans. Faraday Soc. **34**, 1445 (1938).

[3] E.g., E. A. Guggenheim, Proc. Roy. Soc. (London) **A148**, 304 (1935); J. Hirschfelder, D. Stevenson, and H. Eyring, J. Chem. Phys. **5**, 896 (1937).

[4] R. P. Bell, Trans. Faraday Soc. **33**, 496 (1937).

[5] (a) G. Scatchard, S. E. Wood, and J. M. Mochel, J. Phys. Chem. **43**, 119 (1939). (b) G. Scatchard, S. E. Wood, and J. M. Mochel, J. Am. Chem. Soc. **61**, 3206 (1939). (c) G. Scatchard, S. E. Wood, and J. M. Mochel, *ibid.*, **62**, 712 (1940). (d) G. Scatchard and C. L. Raymond, *ibid.* **60**, 1278 (1938). (e) J. R. Lacher and R. E. Hunt, *ibid.* **63**, 1752 (1941). (f) J. R. Lacher, W. B. Buck, and W. H. Parry, *ibid.* **63**, 2422 (1941).

DERIVATION OF EQUATIONS

In order to study solutions by the methods we have been developing, it is convenient, as before, to start with a gaseous mixture and use the rigorous isothermal equation

$$\Delta S = S_g - S_l = R \ln [V_g/\gamma V_f] \qquad \text{I (50)}$$

to get across to the liquid. V_g is the volume of the gas, and V_f is the free volume in the liquid; γ is a "free angle ratio." We may recall that V_f is always defined in terms of the geometrical mean of the momentary v's (box volumes) of all the molecules. Nothing is changed, then, in essence, in going to systems in which molecules of more than one type are present. Since even d' in II (5) is an average, (5), (6), and (3) of II can be used as before to derive

$$V_f = \frac{fb^3g^3}{h^3n^3} V_l \left[\frac{RT}{\Delta E_v}\right]^3; \quad \gamma V_f = \beta V_l \left[\frac{RT}{\Delta E_v}\right]^3 \qquad \text{II (10)}$$

as before, where V_l is the volume of the liquid, ΔE_v its molal energy of vaporization, and f, b, g, h, and n are numbers. It will be seen from their definitions in II that in addition to ΔE, f, b, g, h, n, and γ all have meanings in a binary solution, as averages, which are just as good as those they have in pure liquids. β is defined as $(\gamma f b^3 g^3)/(h^3 n^3)$ and for normal liquids has values at 25°C between 2 and 10, roughly. For a mixture it will be expected to vary smoothly as the composition is changed. We shall use the substitution

$$\beta = \beta_1^{N_1} \times \beta_2^{N_2}, \qquad (1)$$

where N_1 and N_2 are the respective mole fractions. The significance of this is discussed below.

Now for a binary gas mixture we may write[6]

$$S = n_1 R \left[\ln \frac{Q_1' V}{n_1 N} + T \frac{d \ln Q_1'}{dT} + 1\right] + n_2 R \left[\ln \frac{Q_2' V}{n_2 N} + T \frac{d \ln Q_2'}{dT} + 1\right], \qquad (2)$$

where n_1 and n_2 are numbers of moles, Q' is the partition function (for one molecule) without the volume factor, N is Avogadro's number, and the other symbols have obvious meanings. This can

[6] Cf., for example, J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (New York, 1940), Chapter 6.

be written

$$S=n_1B_1(T)+n_1R\ln\frac{V}{n_1}+n_2B_2(T)+n_2R\ln\frac{V}{n_2}$$

$$=n_1B_1(T)+n_2B_2(T)+(n_1+n_2)R\ln\frac{V}{n_1+n_2}$$

$$-n_1R\ln N_1-n_2R\ln N_2, \quad (3)$$

or,

$$S=N_1B_1(T)+N_2B_2(T)+R\ln V_g$$

$$-N_1R\ln N_1-N_2R\ln N_2,$$

S, V, etc. being molal quantities, and N_1, N_2 mole fractions, following the notation of Lewis and Randall.[7] Then, by I (50), for the complete condensation of a mixture of n_1 moles of A and n_2 moles of B,

$$\Delta S=S_l-S_g=(n_1+n_2)R\ln\frac{\gamma V_f}{V_g}$$

$$=(n_1+n_2)R\ln\frac{\gamma V_f}{V_g}, \quad (4)$$

whence

$$S_l=(n_1+n_2)\mathcal{S}_l=(n_1+n_2)[N_1B_1(T)+N_2B_2(T)$$

$$+R\ln(\gamma V_f)-R\Sigma N_i\ln N_i].$$

Inserting II (10)

$$S_l=(n_1+n_2)\mathcal{S}_l=(n_1+n_2)[N_1B_1(T)$$

$$+N_2B_2(T)+R\ln V_l+R\ln\beta$$

$$+3R\ln RT-3R\ln\Delta E_v-R\Sigma N_i\ln N_i]. \quad (5)$$

Here ΔE_v, the molal energy of vaporization of the liquid mixture, is the internal energy liberated in the condensation process considered, and equals

$$\Delta E_v=E_g-N_1\bar{E}_1-N_2\bar{E}_2. \quad (6)$$

We also recall that $V_l=N_1\bar{V}_1+N_2\bar{V}_2$.

We may now differentiate for $\bar{\mathcal{S}}_1$ in the liquid mixture, obtaining

$$\bar{\mathcal{S}}_1=\frac{\partial S_l}{\partial n_1}=\mathcal{S}_l+(n_1+n_2)\frac{\partial \mathcal{S}_l}{\partial n_1}=\mathcal{S}_l+N_2\frac{\partial \mathcal{S}_l}{\partial N_1}$$

$$=\mathcal{S}_l+N_2\left[B_1(T)-B_2(T)+R\frac{\bar{V}_1-\bar{V}_2}{V_l}+R\ln\beta_1\right.$$

$$\left.-R\ln\beta_2+3R\frac{\bar{E}_1-\bar{E}_2}{\Delta E_v}+R\ln\frac{N_2}{N_1}\right], \quad (7)$$

[7] G. N. Lewis and M. Randall, *Thermodynamics* (New York, 1923).

$$=B_1(T)+3R\ln RT+R\ln\beta_1+R\ln V_l$$

$$-3R\ln\Delta E+R\frac{\bar{V}_1-V_l}{V_l}$$

$$+3R\frac{\bar{E}_1-E_l}{\Delta E}-R\ln N_1. \quad (8)$$

(Henceforth ΔE will be written instead of ΔE_v.) In obtaining (7) and (8) we have used (1) and treated $\ln\beta_1$ and $\ln\beta_2$ as partial molal quantities (see below). For the pure substance A,

$$S_1^\circ=B_1(T)+R\ln\beta_1^\circ+R\ln V_1^\circ$$

$$+3R\ln RT-3R\ln\Delta E_1^\circ,$$

so that

$$\bar{S}_1-S_1^\circ=-R\ln N_1+R\ln\frac{\beta_1}{\beta_1^\circ}+R\ln\frac{V_l}{V_1^\circ}$$

$$-3R\ln\frac{\Delta E}{\Delta E_1^\circ}+R\frac{\bar{V}_1-V_l}{V_l}+3R\frac{\bar{E}_1-E_l}{\Delta E}. \quad (9)$$

Using (9) and the corresponding equation for $\bar{S}_2-S_2^\circ$, we may obtain an expression for the entropy of formation of a binary liquid solution

$$\Delta S=S_l-N_1S_1^\circ-N_2S_2^\circ=-N_1R\ln N_1$$

$$-N_2R\ln N_2+N_1R\ln\frac{\beta_1}{\beta_1^\circ}+N_2R\ln\frac{\beta_2}{\beta_2^\circ}$$

$$+R\ln\frac{V_l}{V_1^{\circ N_1}V_2^{\circ N_2}}-3R\ln\frac{\Delta E}{\Delta E_1^{\circ N_1}\Delta E_2^{\circ N_2}},$$

the other terms cancelling, or

$$\Delta S+R\Sigma N_i\ln N_i$$

$$=R\ln\frac{\beta}{\bar{\beta}}+R\ln\frac{V_l}{\bar{V}}-3R\ln\frac{\Delta E}{\overline{\Delta E}}, \quad (10)$$

$$\bar{\beta}=\beta_1^{\circ N_1}\beta_2^{\circ N_2};\quad \bar{V}=V_1^{\circ N_1}V_2^{\circ N_2};$$

$$\overline{\Delta E}=\Delta E_1^{\circ N_1}\Delta E_2^{\circ N_2}. \quad (11)$$

Equation (10), which might have been inferred from (5) by inspection, states that the entropy of formation of a binary liquid mixture deviates from the ideal entropy of mixing by an amount determined by the deviation of β, V_l, and ΔE taken for the solution, from the logarithmic means of these quantities for the pure components.

TABLE I.

Energies, volumes, and excess entropies of mixing for equimolal solutions.[a]

Pair	$C_6H_6-C_6H_{12}$	$CCl_4-C_6H_{12}$	$C_6H_6-CCl_4$	$C_2H_4Br_2-C_6H_5Cl$	$C_2H_4Br_2-C_3H_7NO_2$	$C_6H_5Cl-C_3H_7NO_2$
$100\ V^M/V^\circ$	0.65	0.16	0.003	0.31	0.10	−0.08
ΔE mixing cal./mole	175.8	34.2	30.2	94	122	29
$T\Delta S^E$ calc. cal./mole	77.3	14.7	12.4	37.2	48.3	11.2
$T\Delta S^E$ exp. cal./mole	101.4	17.5	10.7	46	30	−36

Properties of the pure components.

	C_6H_6	C_6H_{12}	CCl_4	$C_2H_4Br_2$	C_6H_5Cl	$C_3H_7NO_2$
V° cc	89.3	108.6	97.1	87.0	102.7	89.3
ΔE° cal./mole	7460	6600	7170	9450	9510	9780

[a] Data of Scatchard, Lacher and coworkers, see reference 5. $T=30°C$. Calculated values obtained by using Eq. (12).

Except for β, (10) contains only experimental quantities. There seems to be no rigorous way of treating β, but it also seems reasonable to expect the approximate rule $\log\beta=1.57-0.000115\Delta H$, obtained in II for normal liquids, to apply rather well to mixtures of normal substances. That is, if we insert II (21) into (10) we should expect a rule of rather good generality and utility. We can hope that individual deviations from it will be small except in mixtures involving solutions which we have other reasons for considering abnormal.

This assumption (remembering that $\Delta H=\Delta E+RT$, sensibly) gives us

$$\Delta S+R\Sigma N_i\ln N_i=0.000526R(N_1\Delta E_1^\circ+N_2\Delta E_2^\circ-\Delta E)+R\ln\frac{V_l}{\bar{V}}-3R\ln\frac{\Delta E}{\overline{\Delta E}}. \quad (12)$$

COMPARISON WITH EXPERIMENT

The left-hand side of (12) is easily recognized as the non-ideal entropy of formation of the solution ΔS^E, that is, the relative entropy of the solution in excess of the classical entropy of mixing, which is $-R\Sigma N_i\ln N_i$. The accurate work of Scatchard, Wood, and Mochel,[5(a)-(c)] and of Lacher and his co-workers,[5(e),(f)] has established the existence of such excess entropy in binary mixtures of normal liquids. Since V_l, $\bar{V}$, ΔE, and $\overline{\Delta E}$ for the various pairs considered can also be obtained from the published data, an experimental test of (12) is possible, and the result of such a test upon equimolal mixtures for six pairs of liquids is given in Table I.

It will be observed that, with the exception of the pairs containing 1-nitropropane, the values of $T\Delta S^E$ calculated from (12) agree with the experimental ones as to order from larger to smaller, and are remarkably close to them in absolute magnitude. Even for the pair benzene-cyclohexane, where the difference is greatest, it amounts to less than 25 percent of the experimental value and corresponds to only 0.07 e.u.

For the pairs containing nitropropane, (12) gives values of ΔS^E which are too high, and a possible reason is suggested by the fact, pointed out by Lacher, that for the nitropropane-chlorobenzene mixture, both ΔS^E and ΔV of mixing are negative. While we do not go as far as Lacher does in attributing to ΔV the determining influence upon ΔS^E, the negative ΔV in this case calls for comment due to the fact that for the same mixture ΔE (or ΔH) of mixing is positive. In a pure liquid, if a positive ΔE accompanied a negative ΔV at constant temperature, this would mean a net repulsive force between the molecules. Here, we know that for pure chlorobenzene and pure nitropropane the internal pressure is strongly attractive,[8] and it does not seem reasonable to imagine a radical change in force fields when they are mixed. Negative ΔV, however, means that, on the average, the molecular centers of gravity are closer together in the mixture than in the pure liquids. Positive ΔE means that the molecular contacts are not more "intimate" in the sense of compound formation or specific attraction, but rather the reverse. The natural assumption is that the molecules in the mixture somehow tend to pack

[8] J. H. Hildebrand, *Solubility* (New York, 1936), second edition.

together more neatly so as to make more economical use of space. But the magnitude of ΔV depends both on geometrical and on dynamical factors—it will in general be different at room temperature from what it would be at 0°K. If the room temperature contraction were less than the virtual one at 0°K, we would have, as here observed, negative ΔV with positive ΔE. This can be stated differently by saying that the positive ΔE means that the actual contraction which takes place is "too small," so that the mixture is somewhat "expanded" as compared with the pure liquids. The sort of packing which produced this result, however, would reduce the average γ, the ratio which measures the freedom of molecular rotation in the liquid, to a value for the mixture which might be markedly lower than the (geometrical) mean for the pure liquids. This would presumably lower the ratio $\beta/\tilde{\beta}$ below the value provided for in (12), and would account for an experimental value of ΔS^E more negative than the calculated one.

As a matter of fact, what we have previously learned about β prepares us for such specific effects, which may be presumed to be present to a greater or less extent, and with positive or negative sign, in other cases also. Attributing such deviations in β to the factor γ relates this discussion to Scatchard's original suggestion[5(a)] as to the possible cause of the large positive ΔS^E in the benzene-cyclohexane mixture. This can be seen if we put into words the physical interpretation of (12), which asserts the positive ΔH (or ΔE) of mixing (*a*) shows that the free volume cells in the mixture are larger than the (geometrical) mean size in the pure liquids and (*b*) corresponds to a decrease in the interference the molecules suffer in their rotational motion. Scatchard's suggestion was equivalent to saying that the second factor is the dominant one, plus the special assumption—now seen to be unnecessary, and subsequently disproved by him through his studies in the benzene-carbon tetrachloride and cyclohexane-carbon tetrachloride pairs—that the whole effect is caused by "too great" a restriction of rotation in pure benzene and/or pure cyclohexane. Our suggested explanation of the discrepancy between the measured ΔS^E of the benzene-cyclohexane pair and the value calculated from (12) is that for some reason β for the pair is higher than II (21) would predict.

In view of the conditional nature of the dependence of β on ΔH discovered in II, we consider that the results of Table I furnish substantial support to the physical picture of liquids and liquid solutions which underlies (12).

Table II shows corresponding comparisons for three mixtures of ethyl alcohol and chloroform, the data being those of Scatchard and Raymond.[5(d)] For 12 mole percent alcohol, the value of ΔS^E calculated from (12) agrees well with the experimental one, suggesting that when it is dilute enough, alcohol in chloroform behaves about as normally as ethylene bromide in chlorobenzene—both of these pairs are made up of molecules with rather large dipole moments. By the time the mole fraction of alcohol reaches 0.28, however, the specific abnormality of this substance (tendency to form hydrogen bonds) seriously disturbs the agreement, and in 80 mole percent alcohol (12) fails grossly, as was to have been expected. Owing to the hydrogen bonding tendency of the alcohol, it is less easy here than before to interpret the relationship of the sign of ΔV to that of ΔE. It may be remarked that these systems also fail to obey Lacher's rule, set up for those of Table I, that ΔS^E is approximately representable as a linear function of ΔV.

RELATIONSHIP TO IDEAL AND REGULAR SOLUTIONS

If (12) is correct, or even if (10) is correct and the relation of β to $\tilde{\beta}$ is not subject to a very strict, and implausible, condition, it follows that an ideal binary solution[9] can exist only when the

TABLE II.

Energies, volumes, and excess entropies of mixing for alcohol-chloroform mixtures[a]

$N_2(C_2H_5OH)$	0.12	0.28	0.80
$100\ V^M/V^\circ$	0.03	0.00	−0.39
ΔE mixing cal./mole	168.6	156.9	−192.3
$T\Delta S^E$ calc. cal./mole	64.0	48.0	−89.8
$T\Delta S^E$ exp. cal./mole	72.8	−1.8	−267

	$CHCl_3$	C_2H_5OH
V° cc	82.85	58.65
ΔE° cal./mole	6680	9490

[a] Data of Scatchard and Raymond, reference 5(d).

[9] E.g., J. H. Hildebrand, reference 8, Chapter 2.

molal volumes and molal internal energies of the components are equal. Only then can V_l, which, for an ideal solution must equal $N_1V_1^\circ+N_2V_2^\circ$, equal $\bar{V}$, and ΔE equal $\Delta\bar{E}$; and if these conditions are not met, ΔS must differ from the ideal entropy of mixing. Another conclusion from (12) is that the non-ideal *regular* solution[10] (one with non-ideal volume and heat change on mixing but with ideal ΔS) cannot exist at all (except for fortuitous cancellations which do not affect the principle). This does not lessen the usefulness of ideal and regular solutions as concepts which provide categories for the classification of real systems. It appears, however, that for estimating activities when values are at hand for ΔH of mixing, entropies based on (12) should be used instead of the assumption of a "regular" ΔS.

The idea that solutions for which ΔE of mixing is not zero should have non-ideal ΔS of formation is, of course, not new. Kirkwood,[11] for example, has shown how a difference in force fields around the two types of molecules produces departure from randomness of configuration, which affects both ΔE and ΔS of mixing. Kirkwood, however, along with others[12] who have calculated such effects, simplified the calculation by considering the distribution of molecules in cells which did not change in size on going from pure liquids to mixtures. It is precisely this change in cell size which we have discussed, together with changes in interference with internal motion. Scatchard[5(a)–(c)] used Kirkwood's equation to compute the entropy anomaly to be expected from the "sorting" effect for some of the systems discussed above and found it, for those cases, to be opposite in sign to the observed effect, and much smaller in magnitude. This indicates that the free volume effect as calculated from (12) is, in solutions of this type, of much the greater importance, as Kirkwood himself concluded on the basis of older data.

It is of interest to note that in principle our Eq. (10) takes implicit account of the "sorting" or non-random distribution effect just discussed. This is because β contains the factor f, which was defined in I and II by the relationship $V_f=Nvf$, where V_f is the molal free volume of the liquid and v the average size of the free volume cell of an individual molecule. f contains contributions for fluctuations, including encroachment of one molecule on the free volume of another. These are determined by the numbers and kinds of microscopic configurations compatible with the total energy of the system, and since the sorting effect consists in a new condition imposed on such compatibility, it will, in principle, show up in f.

In practice, however, we have not been able to predict values of f even in the simplest real systems, and in pure liquids the best we could do was to use entropy data for an empirical determination of β, in which f appears along with other equally troublesome factors. The rough empirical rule II (21) relating β to ΔH_v which we inserted into (10) to obtain (12) therefore takes no account of the sorting effect. As we have seen above, this is of no practical consequence, since the effect is smaller than the uncertainties in the far larger effects which (12) does represent.

DILUTE SOLUTIONS

Changing subscripts in (8) and combining with (3) written for pure substance B in the gas phase gives

$$\Delta S_2=S_{2g}-\bar{S}_2=R\ln V_{2g}-R\ln\beta_2 - R\ln V_l-3R\ln\frac{RT}{\Delta E}+R\frac{V_l-\bar{V}_2}{V_l} +3R\frac{E_l-\bar{E}_2}{\Delta E}+R\ln N_2, \quad (13)$$

as the molal entropy of vaporization of substance B from a solution. If the solution is assumed to be of vanishingly small concentration in B, V_l and ΔE will be the values for pure A. Again, V_{2g} and V_{1g} are the same if the same standard state is used throughout for the gas phase. Substituting V_{1g} for V_{2g} in (13) and using II (14)

$$\Delta S_2=\Delta S_1^\circ-R\ln\frac{\beta_2}{\beta_1^\circ} +R\frac{V_1^\circ-\bar{V}_2}{V_1^\circ}-3R\frac{\Delta E_1^\circ-\Delta E_2}{\Delta E_1^\circ}, \quad (14)$$

[10] J. H. Hildebrand, reference 8, p. 65.
[11] J. G. Kirkwood, J. Phys. Chem. **43**, 97 (1939).
[12] E.g., G. S. Rushbrooke, Proc. Roy. Soc., London **A166**, 296 (1938).

where ΔS_2 is the change of entropy and ΔE_2 the increase in internal energy when one mole of substance B is vaporized from infinitely dilute solution in liquid A, the standard state of the vapor being a partial pressure of 1 atmosphere, and that of the solute a hypothetical mole fraction of unity. Use has again been made of the convention that $E \equiv 0$ for a gas, so that $\Delta E_1 = -E_l$, and $\Delta E_2 = -\bar{E}_2$.

(14) shows that the entropy change considered should differ from the entropy of vaporization of the pure solvent by an amount determined by the relative values of β_2 and β_1°, $\bar{V}_2$ and V_1°, and ΔE_2 and ΔE_1°. Before it can be tested against experimental data, it is necessary to make a substitution for $\ln \beta_2$. Here again, as in interpreting (11), we can give no rigorous treatment, but shall use II (21) to represent the dependence of $\ln \beta_2$ on ΔE_2. Here it is necessary to point out that $\ln \beta_2$, as we have defined it, is a *partial molal* quantity. For according to (1)

$$(n_1+n_2) \ln \beta = n_1 \ln \beta_1 + n_2 \ln \beta_2, \qquad (15)$$

and in obtaining (7) we have assumed that

$$N_1 d \ln \beta_1 + N_2 d \ln \beta_2 = 0; \qquad (16)$$

(16) can be justified both on the grounds that any other assumption would be equally arbitrary, and also by analogy with the exact equation

$$N_1 d\bar{S}_1 + N_2 d\bar{S}_2 = 0,$$

since $\ln \beta_1$ appears in (8) as an additive term in $\bar{S}_1$. Having made this assumption, $\ln \beta_2$ is the rate of change of the extensive quantity $(n_1+n_2) \ln \beta$ with the number of moles of substance B added to the solution, and in (14) $\ln \beta_2$ is the molal rate of change of $(n_1+n_2) \ln \beta$ as an infinitesimal amount of solute is added to the pure solvent. Correspondingly, $\Delta E_2 = -\bar{E}_2$, where $\bar{E}_2$ is the molal rate of change of the internal energy as an infinitesimal amount of solute is added to the solvent.

Proceeding as before, then,

$$\Delta S_2 = \Delta S_1^\circ - 0.000526R[\Delta E_1^\circ - \Delta E_2] + R\frac{V_1^\circ - \bar{V}_2}{V_1^\circ} - 3R\frac{\Delta E_1^\circ - \Delta E_2}{\Delta E_1^\circ}, \qquad (17)$$

or, numerically,

$$\Delta S_2 = \Delta S_1^\circ - 0.001045[\Delta E_1^\circ - \Delta E_2] + 1.986\frac{V_1^\circ - \bar{V}_2}{V_1^\circ} - 5.96\frac{\Delta E_1^\circ - \Delta E_2}{\Delta E_1^\circ}. \qquad (18)$$

Since the term in $\bar{V}_2$ is small compared to the others, (18) predicts that ΔS_2 should be, for any one solvent, very close to a linear function of ΔE_2 (and therefore of ΔH_2). It also predicts, however, that both constants in the linear equation should be specific for the solvent employed.

EXPERIMENTAL TEST FOR DILUTE SOLUTIONS

Bell,[4] using the gas-solubility data of Horiuti,[13] has made calculations, and found regularities, which were used by Barclay and Butler[2] in support of their empirical rule that the linear Eq. II (16) which connects ΔS and ΔH of vaporization of pure liquids also represents ΔS_2 and ΔH_2 for these dilute solutions. We have repeated Bell's calculations for the temperatures 25°C and 40°C (Bell chose 20°C and our 25°C results agree closely with his when reduced to his standard states) and have also calculated "predicted" values of ΔS_2, using (18) and Horiuti's values for $\bar{V}_2$ in the same systems. Table III shows a comparison of ΔS_2 values as calculated (*a*) "experimentally," from the temperature dependence of the gas solubilities, (*b*) "theoretically" from (18), and (*c*) by the Barclay-Butler rule, using II (17). Data obtained by Barclay and Butler on various solutes in acetone, and in ethyl alcohol, are also included, the absence of $\bar{V}_2$ data in these cases, however, making it impossible to use (18) here. Figure 1 shows the same results, the experimental values (at 25°C) of ΔS_2 being represented by crosses, those calculated from (18) by circles, and II (17) by the solid lines. Squares represent values for other temperatures.

Here again, considering the extent to which specific effects are expected to appear, we consider that the data, excepting those on SO_2, give full support, both to the physical picture behind (18) and to the Barclay-Butler rule,

[13] J. Horiuti, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **17**, 125 (1931).

TABLE III. Heats (in calories per mole) and entropies (in e.u.) of vaporization of gases from certain non-polar solvents.

Solvent	Solute		ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B−B)
CCl_4[a]	H_2	25°	−1260	11.7	11.2	11.2
		40°	−1380	11.3	10.4	10.5
CCl_4	N_2	25°	−590	12.6	11.8	12.0
		40°	−680	12.3	11.0	11.3
CCl_4	CO	25°	−340	12.9	12.1	12.3
		40°	−390	12.7	11.4	11.7
CCl_4	O_2	25°	−10	13.4	12.7	12.7
		40°	0	13.4	12.1	12.2
CCl_4	CH_4	25°	700	14.0	13.5	13.6
		40°	640	13.8	12.9	13.0
CCl_4	C_2H_6	25°	2710	16.8	16.1	16.1
		40°	2760	16.9	15.5	15.6
CCl_4	C_2H_4	25°	2340	16.2	15.7	15.7
		40°	2540	16.9	15.3	15.2
CCl_4	C_2H_2	25°	2330	16.7	15.8	15.6
		40°	2490	17.2	15.4	15.3
CCl_4	SO_2	25°	5700	24.3	20.4	19.8
		40°	4960	21.9	18.8	18.3
CCl_4	N_2O	20°	2450	16.5		
C_6H_5Cl	H_2	25°	−1240	12.2	13.6	11.2
		40°	−1290	12.1	13.1	10.6
C_6H_5Cl	N_2	25°	−630	13.3	14.0	12.0
		40°	−680	13.1	13.4	11.3
C_6H_5Cl	CO	25°	−290	13.7	14.4	12.5
		40°	−350	13.5	13.9	11.8
C_6H_5Cl	O_2	25°	−110	13.8	14.7	12.6
		40°	−160	13.7	14.2	12.0
C_6H_5Cl	CH_4	25°	610	14.4	15.4	13.5
		40°	560	14.2	14.9	13.0
C_6H_5Cl	C_2H_6	25°	2470	16.7	17.4	15.8
		40°	2360	16.3	16.7	15.1
C_6H_5Cl	C_2H_4	25°	2370	16.7	17.3	15.7
		40°	2130	16.0	16.5	14.8
C_6H_5Cl	C_2H_2	25°	2810	17.8	18.0	16.2
		40°	2670	17.3	17.3	15.5
C_6H_5Cl	SO_2	25°	7370	27.8	23.3	21.9
		40°	6170	23.9	21.5	19.8
C_6H_5Cl	N_2O	20°	2460	16.9		
C_6H_6	H_2	25°	−1460	11.5	11.5	11.0
		40°	−1620	11.0	10.5	10.1
C_6H_6	N_2	25°	−960	12.1	11.8	11.6
		40°	−1070	11.8	10.8	10.9
C_6H_6	CO	25°	−560	12.7	12.3	12.1
		40°	−680	12.3	11.4	11.3
C_6H_6	O_2	25°	−380	12.8	12.7	12.3
		40°	−370	12.9	11.9	11.7
C_6H_6	CH_4	25°	360	13.5	13.5	13.2
		40°	270	12.7	12.7	12.5
C_6H_6	C_2H_6	25°	2250	15.9	15.8	15.5
		40°	2220	15.8	15.0	14.9
C_6H_6	C_2H_4	25°	2180	16.1	15.9	15.5
		40°	2090	15.7	14.9	14.8
C_6H_6	C_2H_2	25°	3170	18.7	17.4	16.7
		40°	3030	18.2	16.5	15.9
C_6H_6	SO_2	25°	6720	25.3	22.2	21.1
		40°	6260	23.7	20.9	19.9
C_6H_6	N_2O	20°	2170	15.9		
C_6H_6[b]	He	20°	−2710	9.6		
C_6H_6[b]	Ne	20°	−2560	9.3		
C_6H_6[b]	A	20°	−860	11.3		
C_6H_6[c]	H_2O	25°	4100	18.4		17.8
$(CH_3)_2CO$	H_2	25°	−1240	11.9	11.8	11.2
		40°	−1290	11.8	11.1	10.6
$(CH_3)_2CO$	N_2	25°	−640	12.8	12.1	12.0
		40°	−720	12.5	11.4	11.3
$(CH_3)_2CO$	CO	25°	−360	13.0	12.6	12.3
		40°	−430	12.8	11.9	11.7
$(CH_3)_2CO$	O_2	25°	−330	13.0	12.8	12.4
		40°	−430	12.6	12.1	11.7
$(CH_3)_2CO$	CH_4	25°	380	13.8	13.5	13.2
		40°	270	13.4	12.8	12.5
$(CH_3)_2CO$	C_2H_6	25°	2090	16.2	15.7	15.3
		40°	2000	15.9	16.0	14.7
$(CH_3)_2CO$	C_2H_4	25°	2180	16.1	15.9	15.5
		40°	2090	16.0	16.3	14.8
$(CH_3)_2CO$	C_2H_2	25°	4100	19.2	19.0	17.8
		40°	4200	19.4	19.7	17.4
$(CH_3)_2CO$	SO_2	25°	3150	11.4	17.8	16.7
		40°	3300	11.9	18.6	16.3
$(CH_3)_2CO$	N_2O	20°	2870	17.7		
$(CH_3)_2CO$[b]	He	20°	−3240	7.2		
$(CH_3)_2CO$[b]	Ne	20°	−1960	10.8		
$(CH_3)_2CO$[b]	A	20°	−740	11.4		
$(CH_3)_2CO$[d]	CS_2	30°	5840	20.6		
$(CH_3)_2CO$[d]	C_6H_6	30°	7740	22.3		

TABLE III.—*Continued.*

Solvent	Solute		ΔH_2	ΔS_2 (exp.)	ΔS_2 (Eq. 18)	ΔS (B−B)
$(CH_3)_2CO$[d]	$CHCl_3$	30°	8690	24.5		
$(CH_3)_2CO$[d]	C_6H_5Cl	30°	9660	24.9		
$CH_3CO_2CH_3$	H_2	25°	−1230	12.0	12.7	11.2
		40°	−1250	11.9	11.7	10.6
$CH_3CO_2CH_3$	N_2	25°	−680	12.5	13.0	11.9
		40°	−740	12.3	11.9	11.3
$CH_3CO_2CH_3$	CO	25°	−340	12.9	13.5	12.3
		40°	−430	12.6	12.4	11.7
$CH_3CO_2CH_3$	O_2	25°	−340	12.8	13.6	12.3
		40°	−390	12.7	12.6	11.7
$CH_3CO_2CH_3$	CH_4	25°	330	13.5	14.9	13.2
		40°	270	13.3	13.4	12.5
$CH_3CO_2CH_3$	C_2H_6	25°	2060	16.0	16.5	15.3
		40°	2230	16.5	15.6	15.0
$CH_3CO_2CH_3$	C_2H_4	25°	2170	16.1	16.8	15.4
		40°	2050	15.8	15.6	14.7
$CH_3CO_2CH_3$	C_2H_2	25°	4450	20.2	20.2	18.3
		40°	4830	21.5	19.8	18.2
$CH_3CO_2CH_3$	SO_2	25°	4140	14.9	19.8	17.9
		40°	4200	15.1	19.0	17.4
$CH_3CO_2CH_3$	N_2O	20°	2890	17.5		
C_2H_5OH[d]	CS_2	30°	6710	24.1		
C_2H_5OH[d]	C_6H_6	30°	8310	26.7		
C_2H_5OH[d]	$CHCl_3$	30°	8910	27.9		
C_2H_5OH[d]	C_6H_5Cl	30°	9980	28.5		
C_2H_5OH[d]	SO_2	30°	6610	24.2		
C_2H_5OH[d]	NH_3	30°	6810	24.6		
C_2H_5OH[d]	CCl_4	30°	7940	25.8		
$(C_2H_5)_2O$	H_2	25°	−1440	9.9	9.8	11.0
$(C_2H_5)_2O$	N_2	25°	−380	12.0	11.1	12.3
$(C_2H_5)_2O$	CO	25°	−100	12.4	11.6	12.6
$(C_2H_5)_2O$	O_2	25°	−10	12.4	11.9	12.7
$(C_2H_5)_2O$	CH_4	25°	800	13.4	13.1	13.8

[a] Unless otherwise indicated, properties listed are calculated from the data of J. Horiuti, Sci. Pap. Inst. Phys. Chem. Research, Tokyo 17, 125 (1931).

Horiuti presents measurements on solubilities of gases and coefficients of dilatation by absorption which permit calculation of ΔH, ΔS_2 (experimental), and ΔS_2 from Eq. (18).

$$\Delta H = RT - RT^2\frac{\partial \ln (\gamma V_l)}{\partial T},$$

$$\Delta S(\text{exp.}) = -R \ln \gamma - RT\frac{\partial \ln (\gamma V_l)}{\partial T} + R \ln RT + R - R \ln V_l,$$

where γ is the Ostwald Solubility Coefficient and V_l is the molal volume of the solvent.

[b] Bell, Trans. Faraday Soc. **33**, 496 (1937).

Bell obtained these values from the work of Lannung (J. Am. Chem. Soc. **52**, 68 (1930)), on the solubilities of the rare gases. Bell's standard state for the gas is the same as ours, but for the solution he employs the state at which concentration of the solution is equal to concentration in the gaseous state. Conversion to our units requires the addition of the term $R \ln RT - R \ln V_l$, or $20.08 - 4.575 \log V_l$, where V_l is the molal volume of the solvent.

[c] *International Critical Tables*, III, 389.

[d] Barclay and Butler, Trans. Faraday Soc. **34**, 1448 (1938).

Standard states of these authors are $N_2 = 1$ for the solution and $p = 1$ mm Hg for the gas. From their values we subtract $R \ln 760 = 13.2$ e.u.

which is seen to include the empirical result that the specificities implied in (18) are not great in dilute solutions of normal substances.

The experimental values of ΔS_2 for SO_2 stand out in striking contrast to the general agreement we have found for "normal" solutes in "normal" solvents. That SO_2 should be more abnormal than the other substances considered is perhaps not surprising in view of the combination it presents of high dipole moment and comparatively small molecular size. It is nevertheless gratifying to find evidence that the abnormality is not random, but is systematic, and a definite property of SO_2. This is provided by Fig. 2, which plots ΔS_2 *vs.* ΔH_2 for SO_2 in the various solvents used by Horiuti. The fact that the values both for 25° and for 40° give a good straight line (excepting an unexplained anomaly in the CCl_4 case) means that a relationship still exists between ΔS_2 and ΔH_2. The difference between these lines and the "expected" Barclay-Butler line measures the extent to which the SO_2 differs from normal substances in this respect.

The SO_2 result is of interest in connection with a conjecture put forward by Bell,[14] who noted that his selection from Horiuti's data gave points which lay in accurate straight lines when plotted for different solutes in the same solvent, and much poorer ones for the same solute in different solvents. This was in contrast with the early result of Evans and Polanyi,[14] who found good regularity for the second type of plotting. Bell's suggestion is that the relative sizes of solvent and solute molecules determine the type of

[14] M. G. Evans and M. Polanyi, Trans. Faraday Soc. **32**, 1333 (1936).

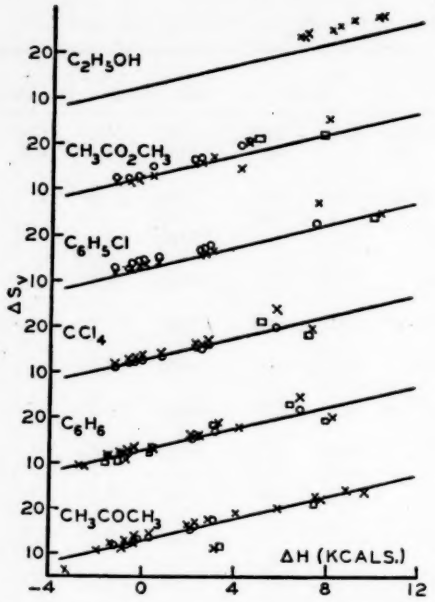

FIG. 1. ΔS_2 *vs.* ΔH^2 for gases in non-polar solvents. The solid line is the revised Barclay-Butler line. Points are from data of Table III.

regularity, so that a good straight line should be obtained for a series of solutes all of which have small molecules, in a solvent made up of larger molecules, or for a single solute of large molecular size in a series of smaller-molecule solvents. The success of Barclay and Butler (the same thing can be seen in Fig. 1) in fitting all of Bell's points to a single straight line shows that with a mole fraction standard state there is not much to choose between the methods of plotting for those solutions. The result found with SO_2, however, raises a similar question. Here the important thing seems to be a specific peculiarity in the force field of the SO_2. Since we are dealing with solutions very dilute in SO_2, it is an individual SO_2 molecule, rather than SO_2 in bulk, to which the peculiarity must be ascribed.

In their plots for solutions in acetone and alcohol, Barclay and Butler remarked that ΔS and ΔH for pure acetone give a point which falls in the line representing solutes in acetone, and pure alcohol falls on the line for alcoholic solutions. (18) gives a reason why this should be true, and Fig. 1 shows that it is true for the other solvents as well. For normal solutes in normal solvents, however, the result is rather trivial, since all of the points fall near the Barclay-Butler line. The alcohol solutions are discussed separately below.

APPARENT FREE VOLUME AND SOLVENT REACTION

The numerical values of ΔS_2 for the permanent gases in normal solvents are of great interest. If the equation

$$\Delta S = R \ln (V_g/\gamma V_f) \qquad \text{I (50)}$$

is applied naively to obtain a value for V_f from the value of ΔS_2 (=11.73 e.u.) for H_2 in CCl_4,

$$\log (\gamma V_f) = 4.389 - (11.73/4.575) = 1.824;$$

$\gamma V_f = 67$ cc approximately. Since $\gamma \leq 1$, this means that on this basis the *apparent* free volume of H_2 is at least 67 cc in a liquid of total volume 96.4 cc (the molal volume of CCl_4). For CH_4 in CCl_4 the corresponding figures are

$$\log (\gamma V_f) = 4.389 - (14.00/4.575) = 1.34;$$

$\gamma V_f = 22$ cc, about. If these values of V_f were for real free volumes, they would mean, for example, that most of the volume of liquid CCl_4 is accessible to H_2 molecules. For H_2 and Ne in benzene, Bell's calculations from Lannung's[15] data give ΔS_2 values which are even worse, as they correspond, on this basis, to a free volume greater than the entire volume of the liquid solvent, i.e., to a net gain in entropy when a given volume of gas dissolves in the same volume of solvent.

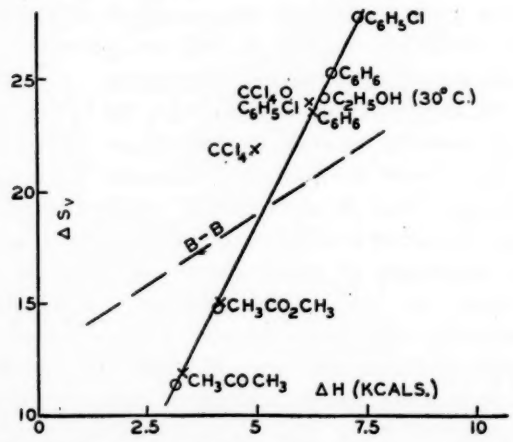

FIG. 2. ΔS_2 *vs.* ΔH_2 for SO_2 in non-polar solvents. The Barclay-Butler curve is indicated by the broken line. 25° values are indicated by circles, 40° values by crosses.

[15] A. Lannung, J. Am. Chem. Soc. **52**, 68 (1930).

This apparent paradox is easily resolved by making a more realistic application of the general principles of I, and writing

$$\Delta S = R \ln \frac{V_g^{n_B}(\gamma V_f)_A{}^{n_A}}{(\gamma V_f)_B{}^{n_B}(\gamma V_f)_A{}^{n_A}} \qquad (19)$$

for the process of removing n_B moles of solute from the dilute solution considered and obtaining as a final state n_A moles of pure liquid solvent and n_B moles of solute as perfect gas. ΔS can be interpreted rigorously in terms of free volumes only when these are the logarithmic means of the free volumes of all of the molecules involved in the process. When we so interpret it, we are able to understand the otherwise very peculiar apparent free volumes obtained above. What happens physically is that when a gas molecule enters the liquid it enters a state of great confinement. This by itself would produce a loss in entropy, perhaps somewhat less than the loss when a molecule of the solvent condenses from vapor to liquid, but hardly more than 3 or 4 e.u. less. The solvent molecules which the gas molecule now has as its neighbors, however, find themselves under less restraint than before. This is reflected, for example, in the fact that $\bar{V}_2$ of H_2 in CCl_4 at 25° is 41 cc. That is, when a molecule of H_2 enters it, the liquid increases in volume almost half as much as when a CCl_4 molecule enters it. Since an H_2 molecule does not "occupy" anything like this volume, a considerable part of $\bar{V}_2$ is a local expansion of the solvent. The forces acting on the neighboring CCl_4 molecules are weaker than before, and this permits them to vibrate in an effectively larger space, and therefore also to rotate somewhat more freely. This results in a gain in entropy, and for H_2 and CH_4 in CCl_4 this solvent reaction almost (and for He and Ne in benzene it more than) compensates for the effect of confinement of the solute molecule. Due to the occurrence of partial molal quantities in it, (18) includes this solvent reaction.

Since the idea of solvent reaction is an important one, we may attempt a rough estimate of the magnitude of the effect in the solutions of normal solutes in normal solvents which we have been considering. The entropy of vaporization of pure CCl_4 is 22.3 e.u. This means that if H_2 in CCl_4 had the same free volume as CCl_4 itself has, and if there were no solvent reaction, ΔS_2 for H_2 in CCl_4 would be 22.3 e.u. Now H_2, being a much smaller molecule, will be expected to be able to "fill crevices" much better than CCl_4 can, which will increase the size of its free volume box. One would guess that a factor of 2 would be too small to represent this effect, but that a factor of 10 would be ample. To be on the safe side, we allow 5 e.u. corresponding to a free volume cell for H_2 somewhat more than 10 times the size of the cell for CCl_4. Since the vibrations in a condensed system are coupled, a separate consideration of the motion of the H_2 without taking account of that of its CCl_4 neighbors is very arbitrary, and, strictly, or thermodynamically, no separation of these motions is possible. It is still instructive, however, to compare the "hypothetical" ΔS_2 of 17.3 e.u., obtained by subtracting the 5 units just discussed from $\Delta S_1°$, with the experimental one of 11.7 e.u. Such a comparison suggests that something like 5.5 e.u. of entropy in the solution must be ascribed to the extra freedom of CCl_4 molecules which we have been discussing.

ALCOHOLIC SOLUTIONS

In II it was found that when water, alcohols, and amines are plotted in the Barclay-Butler diagram for pure liquids, they give points which fall above the standard line, but within 2 e.u. or so of it, and it was remarked that this deviation is rather smaller than might have been expected. A similar comparison for solutions can be seen in Fig. 1. Here, as before, the difference amounts to some 2 e.u., ΔS of vaporization from alcohol being larger.

As remarked above, the fact that ΔS for a pure solvent lies on the line which represents ΔS_2 for solutes dissolved in it agrees with (18), in which ΔS_2 "starts out," as it were, from $\Delta S_1°$ as a point of reference. As a matter of fact, (18) suggests that the abnormality of alcohol as a solvent is to be looked for not in the distance between the alcohol line and the normal line, but in the difference in slopes of the lines. Figure 1 shows that this difference is not great—indeed it is not greater than the differences between the slopes of the corresponding lines drawn for non-polar solvents. We are led to the somewhat surprising

TABLE IV. Heats and entropies of vaporization of gases from aqueous solution.

Solute	Temp.	ΔH	$\Delta S°$
H_2	25°[a]	1280	26.0
	40°[b]	426	23.7
	80°[b]	−170	21.8
N_2	25°[a]	2140	29.8
	40°[b]	1990	29.3
	80°	180	23.9
CO	25°[a]	3910	29.8
	40°[b]	1970	28.5
	80°[b]	10	22.6
O_2	25°[a]	2990	31.3
	40°[b]	2070	30.1
NO	25°[a]	2680	29.4
	40°[b]	2270	28.1
CO_2	25°[a]	4730	30.6
	40°[b]	3870	28.2
COS[a]	25°	5800	35.1
N_2O[a]	25°	4840	31.6
CH_4[a]	25°	3180	31.8
C_2H_6	25°	4430	35.4
C_2H_4[a]	25°	3790	31.3
C_2H_2[a]	25°	3360	25.6
He[c]	25°	840	26.5
	50°	710	26.1
	80°	550	25.5
Ne[c]	25°	1880	28.8
	50°	1280	26.6
	80°	580	24.7
A[c]	25°	2730	30.2
	50°	1840	27.2
	80°	710	23.5
Kr[c]	25°	3550	32.3
	50°	2350	27.8
	80°	740	23.2
Xe[c]	25°	4490	33.6
	50°	2680	28.0
	80°	720	22.1
Rn[c]	25°	5050	34.3
	50°	3100	28.2
	80°	720	21.1
Methyl alcohol[a]	25°	11240	35.0
Ethyl alcohol[a]	25°	12880	40.8
n-Propyl alcohol[a]	25°	14420	46.5
iso-Propyl alcohol[a]	25°	13450	43.5
n-Butyl alcohol[a]	25°	15940	52.0
iso-Butyl alcohol[a]	25°	15240	50.4
sec-Butyl alcohol[a]	25°	15060	49.4
tert-Propyl alcohol[a]	25°	14440	47.6
n-amyl alcohol[a]	25°	17500	58.0
tert-amyl alcohol[a]	25°	15690	52.1
ethyl amine[a]	25°	12910	42.2
ethyl acetate[a]	25°	11710	43.1
Di-ethyl ether[a]	25°	12760	50.5
acetone[a]	25°	10090	35.1
glycerol[a]	25°	24730	66.8
chloroform[a]	25°	9800	43.8
NH_3[d]	25°	5040	20.4

[a] Butler, Trans. Faraday Soc. **33**, 235 (1937).
Butler employs as standard states $N_2=1$ for the solution and $p=1$ mm Hg for the gas. Translation to our standard states of $N_2=1$ and $p=1$ atmosphere requires subtraction of the term $R \ln 760 = 13.2$ e.u. from Butler's values.

[b] Landolt-Bornstein, fifth edition, Vol. I, p. 762, list α the Bunsen absorption coefficient, the volume of gas when reduced to 0° and 760 mm, absorbed by one volume of water when the partial pressure of the gas amounts to 760 mm. We convert α to γ the Ostwald solubility coefficient and employ this coefficient in the following equations to obtain ΔH and ΔS:

$$\Delta H = RT - RT^2 \frac{\partial \ln (\gamma V_l)}{\partial T},$$

$$\Delta S = -R \ln \gamma - RT \frac{\partial \ln (\gamma V_l)}{\partial T} + R \ln RT + R - R \ln v_l.$$

[c] D. D. Eley, Trans. Faraday Soc. **35**, 1283 (1939).
Eley's standard states are 1 atmosphere pressure for the gas and a concentration of one mole per liter for the solution. Therefore to Eley's values we add $R \ln 18/1000 = 8.0$ e.u.

[d] Landolt-Bornstein, fifth edition, supplement 1, p. 764.

conclusion that the interaction between ethyl alcohol and the solutes dissolved in it produces, at infinite dilution, an entropy effect which is not very different, in its relation to the heat of solution, from what is found with a normal solvent. It is true that when argon, for example, dissolves in alcohol, the Ostwald solubility coefficient is very different from that, say, in benzene. And when the temperature variations in these solubility coefficients are used to get ΔS values, the two solutions will give quite different results. We have seen, however, that reduction to a mole fraction basis (the Ostwald coefficients give a volume basis in the first instance) is necessary before the figures will be comparable. We have also seen that as between, say, benzene and

carbon tetrachloride as solvents, the difference in $\Delta S_1°$ must also be taken into account. What we are now saying is that when the corresponding difference is taken into account between the solution in alcohol and that in benzene, and the ΔS_2 values are plotted against ΔH_2, the agreement in behavior as solvents between benzene and alcohol is as good as that between benzene and carbon tetrachloride. This is a rather remarkable result, and means that, in this sense, and for these solutes, the Barclay-Butler rule has succeeded in throwing onto ΔH of formation the entire burden of the abnormality of the alcoholic solutions.

AQUEOUS SOLUTIONS OF NON-ELECTROLYTES

Really striking deviations from the "standard" behavior we have been describing and interpreting are found in the data for aqueous solutions listed in Table IV and plotted in Fig. 3. These are, again, values for molal ΔS and ΔH of vaporization of various non-ionic solutes from infinitely dilute water solutions at 25°C calculated to the standard states of 1 atmosphere for the gases or vapors, and a hypothetical mole fraction of unity in solution. It appears that there is one rather good straight line which represents non-polar solutes, and another which represents the alcohols and amines, while several solutes of intermediate polarity fall between these two lines. Three important features stand out in connection with the line for non-polar solutes. First, all of the ΔS_2 values are "too high" by amounts in excess of 10 e.u.; second, the slope of the line is about half again as great as that of the "standard" one (0.0019 *vs.* 0.00124); third, the line comes nowhere near to the point for $\Delta S_1°$ of pure water. A fourth distinctive feature of these solutions, to which we shall return shortly, is the way they respond to temperature changes. It is clear that some new influence is at work here, and comparison with the results for SO_2 and for alcoholic solutions makes it clear that this is related in some unique way to the properties of water. That it is related to the properties of water in bulk and does not operate on isolated water molecules is clear from the discussion below, but also follows from the normal behavior of water as a solute in benzene, Table III and Fig. 1.

The values of ΔS_2 and ΔH_2 for the solutions of the rare gases in water have been calculated before, by Lange and Watzel[16] and by Eley[17] as well as by Butler,[18] though only in the last of these papers does any attention seem to have been called to the remarkable nature of the results. In all three cases, the calculations were made from the values given by Valentiner[19] for the solubilities of the gases in water. Since Valentiner's work consisted in smoothing the rather discrepant earlier data, it seems at first somewhat unsafe to draw from it such important conclusions as we shall be led to. On the other hand, independent measurements on methane, ethane, oxygen, etc., give similar results, so that we shall accept Valentiner's figures, and the calculations Eley has based on them.

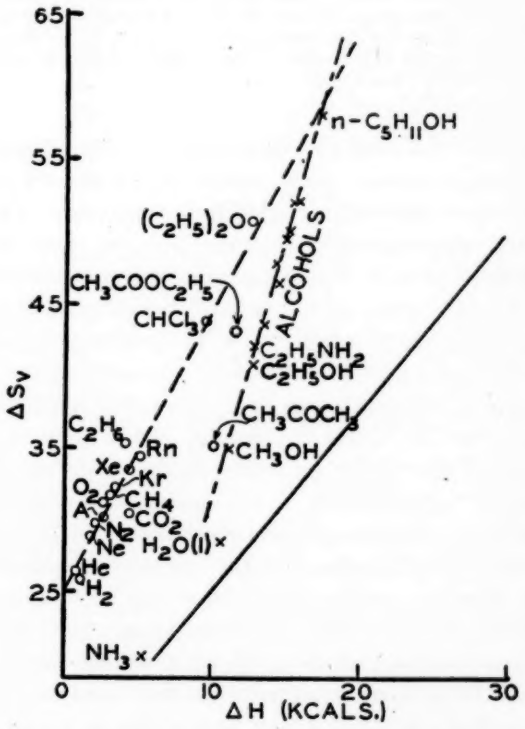

FIG. 3. ΔS_2 for non-ionic solutes in water at 25°C. Data are from Table IV.

[16] E. Lange and R. Watzel, Zeits. f. physik. Chemie **A182**, 1 (1938).
[17] D. D. Eley, Trans. Faraday Soc. **35**, 1281 (1939).
[18] J. A. V. Butler, Trans. Faraday Soc. **33**, 229 (1937); J. A. V. Butler and W. S. Reid, J. Chem. Soc. London, 1171 (1936).
[19] S. Valentiner, Zeits. f. Physik **42**, 253 (1927).

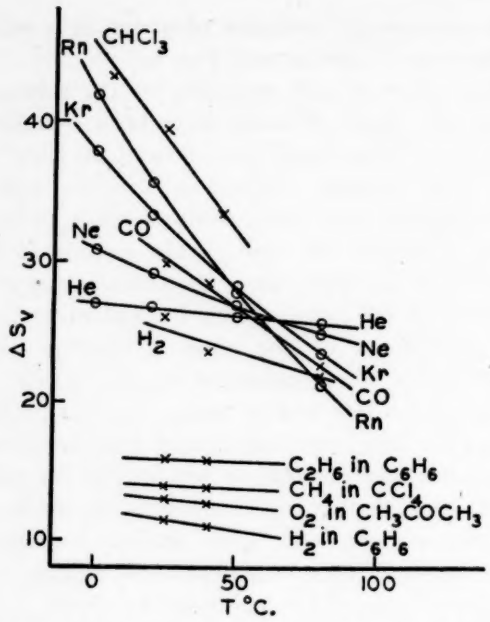

FIG. 4. ΔS_2 *vs.* temperature for gases in water. A number of gases in non-polar solvents have been included for comparison. Values for the rare gases were taken from Eley's paper (reference 17), the correcting factor of R ln (18/1000) being added to his values.

Figure 4 shows ΔS_2 values plotted for a series of temperatures, with values for solutions in non-polar solvents included for comparison. The effect of temperature changes on the aqueous solutions is no less striking than the comparison of the 25° values with "normal" behavior. Taken together, they seem to lead, without much ambiguity, to the following physical picture. When a rare gas atom or a non-polar molecule dissolves in water at room temperature it modifies the water structure in the direction of greater "crystallinity"— the water, so to speak, builds a microscopic iceberg around it.* The extent of this iceberg is the greater the larger the foreign atom. This "freezing" of water produced by the rare gas atom causes heat and entropy to be lost, beyond what would "otherwise" have been expected. The heat adds on to the otherwise smaller heat of solution of the gas, producing the rather considerable positive ΔH of vaporization. The loss in entropy is what causes ΔS of vaporization to be so remarkably large. As the temperature is raised, these icebergs melt, giving rise to the enormous partial molal heat capacity of these gases in water, which may exceed 60 cal./deg./mole. The magnitude of this effect naturally depends on the size of the iceberg originally present, so it is greatest in Rn, and at the higher temperatures the order of ΔS_2 for the rare gases has actually reversed itself, ΔS of vaporization of Rn being smaller than that of He. This presumably means that here the expansion of the system by intrusion of a radon atom loosens the water considerably more than with helium, and the resulting gain in entropy of the system shows up in the lower value of ΔS_2. This corresponds to the "ordinary" solvent reaction which we found in non-polar solvents. Such a tendency should also exist in cold water, where, however, it is overshadowed by the iceberg effect. At still higher temperatures ΔH_2 becomes negative; the solubility of most gases in water shows a minimum when plotted against temperature. This means that at these temperatures the structure of water has been broken down so far as to remove most of its peculiarity as a solvent, and agrees with the x-ray[20] and Raman effect[21] findings on the effect of temperature on the structure of water.

The assumption that the rare gases and hydrocarbon gases form icebergs when they dissolve in cold water receives some support from the existence of crystalline hydrates of these substances. There is, of course, no general correlation between solute species and solid phases (cf. Na_2SO_4 solution above and below the temperature of transition between Na_2SO_4 and $Na_2SO_4 \cdot 10\,H_2O$), but in the case, for example, of the rare gases,[22] or of hydrocarbons,[23] the existence of solid hydrates indicates at any rate that the geometric and energetic relations between the non-polar solute and the water molecules involve no innate antagonism to complex formation.

* Throughout the rest of this paper we shall use the word iceberg, without quotation marks or apology, to represent a microscopic region, either of pure water or surrounding a solute molecule or ion, in which water molecules are tied together in some sort of quasi-solid structure. It is not implied that the structure is exactly ice-like, nor is it necessarily the same in every case where the word iceberg is used.

[20] J. Morgan and B. E. Warren, J. Chem. Phys. **6**, 666 (1938).
[21] P. C. Cross, J. Burnham, and P. A. Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).
[22] R. de. Forcrand, Comptes rendus **135**, 950 (1902), **176**, 355 (1923).
[23] E.g., E. G. Hammerschmidt, Ind. Eng. Chem. **26**, 851 (1934).

The assumption of iceberg formation gives a pictorial interpretation for the observation of Butler[18] that the insolubility of non-polar substances in water is an entropy, rather than an energy phenomenon. Large non-polar molecules have stronger van der Waals force fields around them than do small ones, and are more strongly held in any condensed phase, including aqueous solutions. The larger they are, however, the larger the icebergs which they produce in water, and therefore the greater the loss in entropy involved in dissolving them. Butler's series of values for ΔH_2 and ΔS_2 for the alcohols in water is very instructive in this connection. These give a line (mentioned above) which does not come far from passing through $\Delta S_1°$ for water. CH_3OH has about the same ΔS_2 value as C_2H_6. This is presumably only partly due to iceberg formation in the case of CH_3OH, however, part of the effect being also attributable to the hydrogen bonds which it itself forms. But this hydrogen bonding produces a much larger ΔH_2 than is found for C_2H_6, shifting the CH_3OH point to the right in the plot (Fig. 3). The relative importance of hydrogen bonding (of the solutes) and iceberg formation shifts in favor of the latter as the hydrocarbon chain of the alcohol increases, and the points for the higher alchols fall progressively closer and closer to the non-polar solute line, finally coming very near to it for amyl alcohol.

It may be permissible at this point to speculate as to the "cause" of iceberg formation when a non-polar solute molecule dissolves in water. While we have not succeeded in formulating any very satisfactory detailed picture, a rather suggestive idea is that this is an example of a sort of microscopic operation of the Le Chatelier principle. Any solute molecule occupies a space that is large compared with what would be required if it were not there, and therefore even helium causes the water to expand somewhat. Cold water is unique in that there exists in it a mobile equilibrium between different structures,[24] in which there are probably several structures represented by moderately large populations. One of these structures is more open than any other and it seems reasonable to imagine that at the edge of a patch of this material there is a greater proportion of "available" space than elsewhere. We might therefore expect a foreign molecule to find its way to such an edge location, and to stabilize it to such effect as to increase the population of the iceberg material. Such icebergs might or might not fuse together about the solute molecule.

[24] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

IONIC SOLUTIONS

Another remarkable phenomenon appears when the heats and entropies of hydration of rare gas ions are listed, as in Table V, and com-

TABLE V. Ionic solutes in aqueous solution.

Ion	ΔH [a]	ΔS_v [b]	ΔS^{el} [c]	$\Delta_{Bingham}$ [d]
F^-	122.6	40.9	+3.5	−13.6
Cl^-	88.7	26.6	−10.2	+0.28
Br^-	81.4	22.7	−13.9	+3.09
I^-	72.1	18.5	−17.9	7.58
NO_3^-		26.8 (16.8)	−19.4	3.06
Ac^-				−21.4
SO_4^{--}		56.4 (50)		−20.4
H^+		38.6		−6.41
Li^+	121.2	39.6	+1.1	−14.0
Na^+	94.6	33.9	−4.0	−9.60
K^+	75.8	25.3	−12.0	+0.28
Rb^+	69.2	23.1	−14.1	1.86
Cs^+	62.0	21.3	−15.7	2.59
NH_4^+		30.5 (25.5)	−11.7	+0.44
Mg^{++}		84.2		−36.5
Cu^{++}		82.0		−34.7
Zn^{++}		81.3		−35.6
Ca^{++}		65.5		−31.3
Sr^{++}		63.7		−28.4
Ba^{++}		55.6		−25.3
Al^{+++}		133.5 (±10)		−70.5
Fe^{+++}		120.5 (±5)		−52.2
$CH_3NH_3^+$				−6.3
$(CH_3)_2NH_2^+$				−10.4
$(CH_3)_3NH^+$				−34.4
$(CH_3)_4N^+$				−14.0
$(C_2H_5)NH_3^+$				−15.2
$(C_2H_5)_2NH_2^+$				−25.7
$(C_2H_5)_3NH^+$				−33.1
$(C_2H_5)_4N^+$				−34.3
$(C_3H_7)_4N^+$				−74.3
$C_6H_5NH_3^+$				−25.6

[a] Molal ΔH of vaporization of ions from aqueous solution at 25°C. Values (in kg cal./mole) taken from W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. 7, 108 (1939).

[b] Molal ΔS of vaporization of ions at 25°C from a hypothetical mole fraction of unity in aqueous solution to a hypothetical gas state at 1 atmosphere pressure. Values (in e.u.) for the monatomic ions were obtained by using the Sackur equation for the gas, and the aqueous entropy data of Latimer, Pitzer, and Smith (see reference 25). The absolute partial molal entropy of Cl^- in hypothetical molal solution is taken as 18.1 e.u. (see reference 26). For NO_3^-, NH_4^+, SO_4^{--}, vibrational and rotational entropies in the gas state were computed using interatomic distances and vibration frequencies as follows: NO_3^-, N−O=1.21A, 720 cm^{-1} (2), 830 cm^{-1}, 1050 cm^{-1}, 1350 cm^{-1} (2) NH_4^+, N−H=1.0A, 1403 (3), 1712 (2), 3043, 3123 (3); SO_4^{--}, S−O=1.5A, 620 (3), 450 (2), 980, 1100 (3). For comparison with monatomic ions, restriction of rotation in the dissolved state was estimated at about 10 e.u. for NO_3^-, 5 e.u. for NH_4^+, and 6 e.u. for SO_4^{--}. The values obtained by subtracting out these quantities are shown in parenthesis.

[c] Hypothetical extra entropy of vaporization (e.u. per mole) due to the effect of the ions in the structure of the solution. Computed by use of Eq. (20).

[d] Molal fluidity elevations of the ions, taken from Bingham (see reference 29).

pared, as in Fig. 5, with the corresponding quantities for non-polar substances. Here ΔS_2 has been computed from the Sackur equation and the S_2 values of Latimer, Pitzer, and Smith,[25] and converted to our standard states, using the Eastman-Young[26] convention that the absolute partial molal entropy of Cl^- is 18.1 e.u. We expect, of course, that the presence of the ionic charge will have a large effect on the energy of the system, and are not surprised to find ΔH values 7 to 10 times as great as those characteristic of non-ionic solutes. The fact that the ΔS_2 values, however, are in exactly the same range (18 to 40 e.u.) as those for the non-polar solutes is less easily predictable. The sort of situation we are confronted with is strikingly illustrated by comparing the loss in entropy on dissolving a K^+ ion and a Cl^- ion, both of which have the electronic structure of argon, with the loss on dissolving two argon atoms in water. The values are $25.3+26.6=51.9$ e.u. and $30.2+30.2=60.4$ e.u., respectively. The effect of the charges is actually to *lessen* the entropy loss. The phenomenon is the more interesting when we remember that Latimer and his co-workers[27] have succeeded in accounting rather well for the entropy loss on dissolving the ions by identifying it with the entropy of polarization of the water by the ionic charges, treating water as a continuous dielectric, as in classical electrolyte theory.

Now while a significant amount, perhaps 10–15 e.u., of the 30.2 e.u. that make up ΔS_2 of argon is iceberg entropy, and therefore roughly comparable to the dielectric lining up of the water molecules by the ionic charge, another important part is caused by the restriction of the argon atom into a free volume box of some sort. Qualitatively, some contribution from this cause must also be present for the ions. When this is added to the dielectric loss, the net expected ΔS_2 for the ions is a good bit larger than the observed value. This is still true when the ion is pictured as freezing the first layer of water molecules into a state of some sort of dielectric saturation (see below). The conclusion is that in an ionic solution there is "too much" entropy, just as in the rare

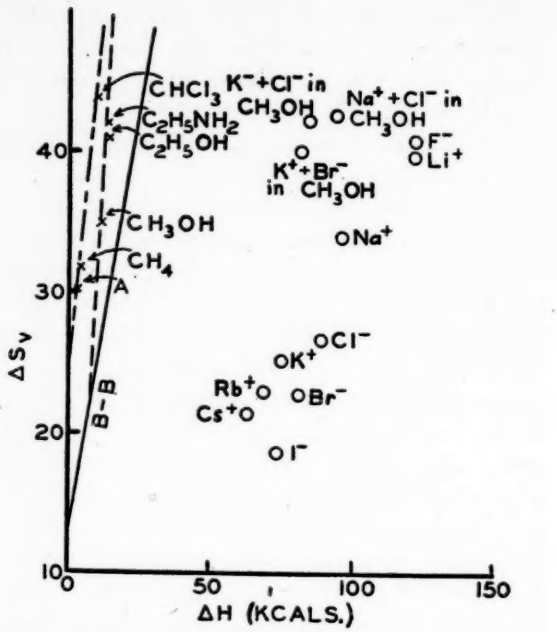

FIG. 5. ΔS_2 *vs.* ΔH_2 for alkali and halide ions in aqueous solution. The Barclay-Butler line, as well as the lines for the rare gases in water and alcohols in water, taken from Fig. 3, have been included. Data are from Table V.

gas solution there was "too little." The probable explanation is that around the ions, beyond the first "saturated" region of water molecules, there is a region or belt in which the water structure is broken down, or melted, or depolymerized, as compared with ordinary water.

Pictorially, this effect of an ion is easy to understand. In the normal 4-coordinated water structure we may think of 5 water molecules in a tetrahedron, one O at the center, with four others in some sort of tetrahedral positions around it. Two of these peripheral oxygens are using "their own" hydrogens to bind them to the central oxygen, while two are held by hydrogens which "belong" to the central water molecule. This means that the kind of tetrahedron which will fit satisfactorily into an extended patch of ice-like water has at two of its corners water molecules which have one type of orientation, while the orientation at the other two corners must be different. Assume now that it is desired to fit a positive ion, Na^+, say, into the structure. The most favorable way to do this will be to give it a coordination shell of four water molecules, and to let these assume positions around it in which the O's are at the corners of a tetrahedron.

[25] W. M. Latimer, K. S. Pitzer, and W. V. Smith, J. Am. Chem. Soc. 60, 1829 (1938).
[26] M. B. Young, Thesis, University of California, 1935.
[27] W. M. Latimer, Chem. Rev. 18, 349 (1936).

But now, even if the resulting tetrahedron is of the right size, it can still not fit well into an iceberg. For there can be little doubt that the strong field of the ionic charge orients all four of the waters the same way (in this case with hydrogens out), instead of two one way and two another as required for a perfect fit. Things will therefore not come out even. When we include the influence of ionic size it is clear that it will be necessary to go out some distance from a positive ion before the water has "recovered itself" sufficiently to have its characteristic structure and entropy. An exactly corresponding discussion can be given for a negative ion and a similar one for the case where more than one layer of water is "frozen" to the ion.

Any attempt to estimate the numerical magnitude of this melting effect must be based on rather arbitrary assumptions for which in the first instance no strict justification can be given. As in the discussion of the solvent reaction when H_2 dissolves in CCl_4, what is involved is an attempt to separate, for our own conceptual convenience, effects which are essentially parts of a single inseparable phenomenon. However, we have a physical picture which furnishes certain categories which must be valid in principle, and it is an instructive exercise in a sort of bookkeeping to attempt to assign appropriate entropy contributions to them. We shall, moreover, find *a posteriori* support for our results.

To begin with, when a gas ion dissolves, it enters a free-volume box, and in our standard states 20–25 e.u. is a sort of "par" value for the corresponding loss of entropy per mole. Since the forces between the ion and its water neighbors are large, we could increase this figure somewhat, but shall, instead, attribute the extra entropy loss to the water, and accept a value of 20 e.u. for the free-volume effect. In considering the solvent reaction, it has been usual to consider it in two parts. We shall need four, but shall begin with the two customary ones. The first is the effect on the first layer of water molecules, and we shall treat this very simply by assuming, as usual, that it contains 4 water molecules (for the univalent ions we are considering) and that each of these, as compared with "ordinary" water, has lost half as much entropy as it would have on freezing to ice. Since ΔS of fusion (calculated as virtual at 25°C) of water is about 6 e.u. per mole, this gives, roughly, 12 e.u. lost by the water in the first layer around the ion. Again as usual, we treat the rest of the water as a polarized dielectric medium. For this, we take Latimer's[27] equation $\Delta S = 22z^2/r$ for the entropy loss (z = ionic charge), using now for r the radius of the ion plus the oxygen-oxygen distance in ice, or $\Delta S_D = 22z^2/(r_i + 2.8)$. We do not know how much error is involved in this approximation, but the effect is in any case of secondary magnitude.

The third solvent reaction effect is the specific influence of the ion on the structure of the water beyond the first layer. We shall call it ΔS^{st} and it will be positive when the net qualitative effect on the structure of the water has been to intensify it, as is the case with rare gas atoms, and negative when there is a net breaking effect—when icebergs have been melted.

Finally, the considerations of the first paper of this series make it clear that a fluctuation term must be added to the entropy of the solution as a whole. This arises because no individual patch of the solution, whether it contain an ion or not, has a structure which is just like that of the average of the solution as a whole, and the possibility of changes in position and extent of the "firmer" and "looser" patches produces extra entropy. Correspondingly, the water around one individual ion will always have a structure which is slightly more or slightly less pronounced than the average for all the ions of that type, and the amount of this variation is related to the "temperature-dependence" entropy discussed in I. Formally, the fluctuation entropy we are now speaking of is represented by a term in $T(d \ln Q)/(dT)$ where Q is the complete partition function of the solution. We have no way of evaluating this, and even if we had it would still be necessary to differentiate it to get the partial molal contribution for the ion under discussion.

We shall therefore have to treat this fluctuation term as we treated similar ones in I and II, and call it a part of ΔS^{st}. This is physically reasonable also, since it is the existence of structure in the solution which gives rise to this particular fluctuation effect, and this fluctuation term is a part of the total "structural entropy" of the solution.

Adding up these guesses, we get, for a singly charged ion,

$$\Delta S_2 = 20+12+\frac{22}{r_i+2.8}+\Delta S^{st}, \qquad (20)$$

whence

$$\Delta S^{st} = \Delta S_2 - 32 - \frac{22}{r_i+2.8}. \qquad (20')$$

Table V gives values of ΔS^{st} computed from (20'), and it will be noted that it makes all of the alkali and halide ions except Li^+ and F^- appear to have a net structure-breaking effect over and above the other things they do when they dissolve in water, and that for the larger ions the effect is considerable.

In practice, (20') makes ΔS^{st} a catch-all which should reflect not only the structural features which it purports to represent, but also any changes from ion to ion in the first-layer freezing and the free-volume contributions. The probable magnitude of such changes is discussed further below. Numerically, however, we may note here that it seems likely that any criticism of the numbers used should result in raising the 12 e.u. and 20 e.u. to larger values. This would make ΔS^{st} still more negative, and would strengthen our contention that a structure-breaking effect occurs. When more is known about the structure of these solutions it will doubtless be clearer how each of the effects discussed contributes to the relationship, discovered by Latimer and his coworkers, between ΔS_2 and the crystallographic radii of the ions.

Mention must be made of the interesting paper of Eley and Evans,[28] in which they attempt to calculate ΔS_2 for monatomic ions. We shall not discuss it in detail, since they did not consider either the structure or the fluctuation terms we have introduced, and their assumptions regarding the free-volume contribution are in conflict with ours. As they themselves state, however, their model is greatly over-simplified, and the importance of their paper lies in pointing out some of the factors which a complete theory must take into account.

TABLE VI. Partial molal heat capacities at infinite dilution.

Solute	$\bar{C}^\circ_{P_2}$ (cal./deg./mole)	Solute	$\bar{C}^\circ_{P_2}$
HCl	−32.5	NaCl	−23.8
HBr	−33.0	NaBr	−24.3
HI	−33.7	NaI	−25.0
LiCl	−16.2	KCl	−29.0
LiBr	−16.7	KBr	−29.5
LiI	−17.4	KI	−30.2

Values calculated by F. D. Rossini, Bur. Stand. J. Research, **7**, 47 (1931).

[28] D. D. Eley and M. G. Evans, Trans. Faraday Soc. **34**, 1093 (1938).

STRUCTURE AND PROPERTIES OF AQUEOUS ELECTROLYTES

If our knowledge of electrolytic solutions were restricted to the information which we have so far adduced, the most that could be said for the values of ΔS^{st} listed in Table V would be that they fall well enough into the general physical picture of entropy changes which we have been developing, and that they are not in conflict with any facts which have come to our attention. They gain very greatly, however, in their claim for serious consideration, when regarded in the light of evidence from (*a*) viscosity and (*b*) heat capacity data.

Bernal and Fowler[24] have called attention, as have earlier workers in more general terms, to the connection between the effect of dissolved ions on the structure of water and their influence on the viscosity, or fluidity, of the solution. Bingham[29] has tabulated the "ionic elevations" (Δ) of fluidity which may be ascribed to the individual ions if K^+ and Cl^- are assumed equivalent (on the basis of their closely equal ionic conductances). Bingham's study is concerned with concentrations high enough ($0.1M$–$1.0M$) for the Jones and Dole[30] term in the square root of concentration to have been completely swamped by the specific linear term. The general agreement with experiment, however, of his fluidity values for various concentrations as calculated from these Δ's makes it appear that they have some meaning for dilute solutions also. Values of Δ quoted from Bingham's paper are listed in Table V. Their parallelism with ΔS^{st} is clear, and will be discussed more fully below. The ions which increase the fluidity of water, presumably by "depolymerization," are ones to which, quali-

[29] E. C. Bingham, J. Phys. Chem. **45**, 885 (1941).

[30] G. Jones and M. Dole, J. Am. Chem. Soc. **51**, 2950 (1929).

tatively, we have ascribed large net structure-breaking effects.

Again, the rather large negative partial molal heat capacities of the ions are well known[31] and attempts[31] have been made to explain them on the basis of the electrostatic picture of the water as a dielectric medium, subject to polarization and electrostriction by the fields of the ions. Qualitatively such a representation, or a more refined one which pictures the effect of the field on water molecules instead of upon a continuous medium, shows that the existence of the strong fields should decrease the heat capacity of the system. On the other hand, it must predict, as an effect of ionic size, and therefore of ionic field, that $\bar{C}_{P_2}°$ of LiCl, for example, should be more negative than that of NaCl, which should, in turn be more negative than that of KCl. Likewise, for the different halides, $\bar{C}_{P_2}°$ should become more negative in the order NaI—NaBr—NaCl. Exactly the reverse is the case, as shown in Table VI, the values being Rossini's[32] virtual ones for infinite dilution. Our picture of the structure of the solution, on the other hand, in analogy with the explanation found for the large positive $\bar{C}_{P_2}$ values of the rare gases, suggests that, since an appreciable part of the heat taken up when cold water is warmed goes to melt icebergs, an ionic solution in which some of the icebergs had already been melted should take up less heat when warmed. This should contribute a negative term to $\bar{C}_{P_2}$ which should be biggest in the cases where the ions had the greatest structure-breaking effect. Comparison of Tables V and VI shows that this is what is observed.

The idea that ions have a depolymerizing effect on water is not new, of course, though we know of no other treatment in which it has been used for the purpose to which we are applying it. It is a part, or a consequence, of Tammann's[33] internal pressure analogy, and can be applied to explain the values of partial molal volumes, expansibilities, compressibilities, etc. In these cases, however, the basis for distinguishing structure-breaking from polarization or electrostriction effects is not clear cut, and this is also true in the interpretation of the effect of salts on the temperature of maximum density. In contrast to this, we feel that the conclusions from viscosity and heat capacity are straight-forward, and signify that there is real physical meaning, both in the concept symbolized by ΔS^{si}, and in the rather large negative values obtained for this quantity in the cases of the larger univalent ions.

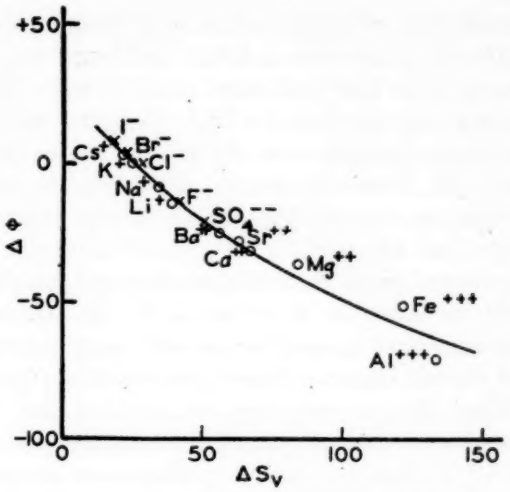

FIG. 6. ΔS_2 in e.u. *vs.* molal fluidity elevation in rhes. Data are from Table V.

A suggestion for a more definite picture of the effect of an ion on the structure of the solution is furnished by Fig. 6, where ΔS of vaporization of the ions is plotted against Bingham's Δ values. The fact that from Li^+ on through Ba^{++}, SO_4^{--}, Mg^{++}, etc., to Al^{+++} the greater and greater ΔS values continue to be accompanied by roughly proportional decrements in fluidity is very striking. (Incidentally, the fact that the positive and negative ions and the ions of different valence give points which fall so nearly on the same curve means either that the Eastman-Latimer[26,27] assumption of -4.6 e.u. for the absolute entropy of H^+, and Bingham's assumption that K^+ and Cl^- have equal effects on fluidity, are both correct, or else that they are in error by compensating amounts.) In going down this series of ions we cannot believe that the large and progressive decrease in fluidity is owing primarily to an effect in the immediate neighborhood of the ion—an effect which is becoming more and more intense. We must rather

[31] See, for example, H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (New York, 1943), Chapter 8, Section 4, for data and bibliography.
[32] F. D. Rossini, Bur. Stand. J. Research **7**, 47 (1931).
[33] G. Tammann, *Über die Beziehung Zwischen den inneren Kräften und Eigenschaften der Lösungen* (Leipzig, 1907).

assume that whatever influence is being exerted by the ion is affecting a larger and larger region around it, so that a solution of Al^{+++} owes both its low entropy and its high viscosity to the existence, around each Al^{+++} ion, of a large patch of "frozen" water. According to this picture, as one goes back up the curve, through Mg^{++} and Li^+ to Cl^-, Cs^+, and I^-, the size of the frozen patch becomes smaller and smaller, until its influence is overcome by the thawed belt outside of it, and the net structural entropy and the net effect on fluidity are both positive.[34]

Now the entropy loss by the ion and its *immediate* water neighbors is probably greater in Al^{+++} than in I^-, but perhaps not tremendously greater, for there are two kinds of saturation which limit the amount of entropy which can be lost in such a region. One is a Debye[35] saturation due to the form of the Langevin[36] function which relates dipole orientation to field strength. The other is a quantum effect as a result of which the effective or virtual free volume box in which a particle vibrates cannot become smaller than a value determined by the uncertainty principle[37]—this is what prevents the entropy contribution $R \ln v$ from becoming negative, as it would if classical laws held in low temperature or high force regions. These two saturation effects bring about a state of affairs in which, since the field near the "surface" of an I^- ion is already very strong—of the order of 10^7 volts per centimeter—even multiplying it by 50, which is about what happens (presumably) in going to Al^{+++}, cannot decrease the entropy of the immediate neighborhood by any enormous amount. The 20 e.u. difference between ΔS_2 for I^- and Li^+, and the nearly 100 e.u. difference between Li^+ and Al^{+++} are therefore to be ascribed largely to spreading out of the frozen region around the ion, along, presumably, with some diminution—perhaps even the disappearance—of the positive entropy contribution from a thawed belt. These changes are properly represented in ΔS^{st}, and the existence of the saturation phenomenon makes (20′) not entirely naive in attempting, as a first approximation, to use the same free-volume and first-layer contributions for all univalent ions, even though 32 e.u. may not necessarily be the right value for the sum of these roughly constant terms.

Two additional types of data lend direct confirmation to the picture we have outlined. One is found in the study by Frank and Robinson[38] of entropies of dilution. This study led them to conclude, as we have done, that each ion has a specific influence on the structure of the solution, and it is noteworthy that the ions to which they ascribed a large structure-breaking effect are just those for which we have found large negative values for ΔS^{st}. For Li^+ they found, as we have done, a net structure-promoting tendency. NH_4^+ in NH_4Cl, however, they found to be structure-promoting, while we, both in respect of ΔS_2 and of Δ, find it to be almost indistinguishable from K^+, which presumably has a net structure-breaking effect. We offer as a tentative explanation of this discrepancy the suggestion that, due to the split charge and hydrogen-bonding faculty of NH_4^+, the type of structural influence it exerts on the water is unusual, producing no regions either of marked freezing or of marked thawing. As the solution becomes more concentrated, it would be necessary to assume that this unusual type of structure around the NH_4^+ was able to some extent to overcome the thawing tendency around the Cl^- ions so as to produce less net structure-breaking in the solution than is found, at the same concentration, with KCl.

Second, a series of investigations which lend very striking support to the iceberg picture are reported by Freed[39] and his co-workers on the line spectra of solutions of europium ion, Eu^{+++}. They found evidence of lattice vibrations coupled with the main electronic transitions, and concluded that the Eu^{+++} ion must be surrounded by a quasi-solid patch of material capable of supporting these vibrations. Freed's comment is: "Although it is too early to be definite as to how far from the europium ions the oscillating units need be assumed to extend in a good approximation, it seems that they extend farther than most of us are prepared to accept at present."

While no ΔS_2 value for Eu^{+++} is available,

[34] Cf. the discussion of Prins (J. Chem. Phys. **3**, 72 (1935)) of "hygroscopic" *vs.* "non-hygroscopic" ions.
[35] P. Debye, *Polare Molekeln* (Leipzig, 1929).
[36] P. Langevin, Ann. Chim. Phys. **8**, 70 (1905).
[37] Cf. J. E. Mayer and M. G. Mayer, reference 6, p. 217.
[38] H. S. Frank and A. L. Robinson, J. Chem. Phys. **8**, 933 (1940). See also literature there cited.
[39] S. Freed, Rev. Mod. Phys. **14**, 105 (1942).

comparison of S_2 values for Al^{+++} and Fe^{+++} suggest an estimate of about 100 e.u. for this quantity. This would correspond to a very considerable frozen patch around the Eu^{+++} ion. While many detailed points remain to be considered it seems reasonable to suggest identifying our iceberg with Freed's oscillating unit.

Finally, there are two other fields in which indirect, but suggestive, support can be found for the picture. We mention, first, the work of Latimer and Slansky[40] on the entropy of solvation of several alkali halides in absolute methanol. Their data (average ΔS_2 for M^+ and X^- against average ΔH_2), which are plotted in Fig. 5, show that on the average about 15 e.u. more entropy are lost on dissolving an ion in methanol than on dissolving it into the same volume of water. We account for $R \ln (32/18) \times (1/0.761) = 1.6$ e.u. of this in the greater mole fraction of solute in the methanol solution. For the balance, we agree with Latimer and Slansky that the methanol can be expected to lose more entropy in the electric field of an ion, but an estimate based on a virtual ΔS of fusion at 25°C, and on a comparison of the temperature dependence of dielectric constant with that of water, indicates that this difference may amount to 10 e.u. or less. As Latimer and Slansky point out, our ignorance of effective ionic radii in methanol solutions makes such a discussion rather speculative, but we suggest that there may well remain a difference which can be accounted for by the fact that no appreciable gain in entropy is to be expected in methanol on the score of structure-breaking, whereas we have estimated that in aqueous solutions this effect has increased S_2 and decreased ΔS of hydration for the larger alkali and halide ions by amounts of from 5 to 10 e.u.

The other speculation is suggested by the negative signs and comparative values of the fluidity elevations listed by Bingham for the alkyl ammonium ions. (Table V) It would be difficult to calculate ΔS_2 values for these ions, and the identification of negative Δ values with iceberg formation is less straightforward here than in the case of a small rare gas ion. The ionic fluidity should, in fact, be affected by size and shape effects on the viscous drag of the ion itself, and comparison of Δ values for mono-, di-, tri- and tetramethyl ammonium ions, and for their ethyl homologues, indicates the existence of specific shape, or hydrogen-bonding, or symmetry effects. The series tetramethyl, tetraethyl, tetrapropyl ammonium ions, however, shows a decrease in Δ which seems too large to be accounted for by effects related to the Stokes Law drag on the "simple" ion. Also, though these data are assembled from several sources, some quite old, the effects are so large as almost certainly to be real. It appears, therefore, that an ion which introduces large non-polar groups into water causes iceberg formation, much as the non-polar groups themselves would do in the absence of the ionic charge.

At first glance this seems inconsistent with the direct variation we have postulated of size of iceberg with ionic potential $\varphi = |z|e/r_i$ from I^- to Al^{+++}. As just suggested, however, the mechanism of iceberg formation with R_4N^+ is comparable to that for C_2H_6, rather than to the quite different thing which Al^{+++} does to water. We therefore accept the conclusion that large icebergs, of different "origin" but with similar entropy and fluidity effects, are formed around ions at both ends of the scale of ionic potential. It is understood, of course, that very small ionic fields can be obtained for this purpose, only by "padding" univalent ions with non-polar groups.

A fact which increases the attractiveness of the idea of icebergs about tetraalkyl ammonium ions is that it fits in with the observation of Fowler, Loebenstein, Pall, and Kraus,[41] that certain tetra *n*-butyl ammonium and tetraisoamyl ammonium salts form "high hydrates"—i.e., crystals containing 18 to 60 molecules of water of crystallization, and melting at from 5° to 40°C. They observed no such hydrates with salts of smaller cations, and it is noteworthy that the largest number of water molecules was found with tetrabutyl ammonium acetate, the acetate ion having the most negative Δ value of the anions they mention, and presumably again owing this large negativity to the presence of a methyl group.

We have had occasion before to recall that there is no general structural connection between

[40] W. M. Latimer and C. M. Slansky, J. Am. Chem. Soc. 62, 2019 (1940).

[41] D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus, J. Am. Chem. Soc. 62, 1140 (1940).

solute species and the solid phases with which they are in equilibrium. In the case, however, of $(n\text{-}C_4H_9)_4NAc \cdot 60\ H_2O$, we find it difficult to see how this crystal would form except through the aggregation of heavily hydrated particles already in existence. It would be most interesting to know the entropy of fusion of this crystal, which melts to a solution of something less than $1M$ concentration. We hazard the conjecture that it is small. If it were necessary to freeze even 50 of the water molecules *in the process of solidification*, ΔS of fusion should be of the order of 300 e.u., and ΔH of the order of 65–70 cal./g. If, however, the freezing of the water is largely complete in the liquid phase, these values should be much lower.*

Our iceberg hypothesis for the tetraalkyl ammonium and acetate ions has a reasonable relationship, also, to the well-known surface activity of higher alkyl ammonium ions and of long-chain fatty acid anions. When the non-polar part of an ion becomes big enough, the ion is forced out of the solution. As pointed out above, this is an entropy effect. It produces a measurable lowering of surface tension even in tetramethyl ammonium halides and in sodium butyrate. The properties we have just been discussing may therefore be regarded as marking the rudiments or preliminaries of detergency. This implies that a complete study of surface phenomena should take explicit account of the effect of solutes on the structure of water.

RELATIONSHIP TO ELECTROLYTE THEORY

If the picture we have been developing of the structure of aqueous solutions of ions is correct, it should have interesting consequences for conventional electrolyte theory, and we conclude this paper with a brief mention of a few possibilities.

* The question arises whether the purely "non-polar" icebergs formed around rare gas atoms and other non-polar molecules influence the fluidity of solutions in the same way as "ionic" icebergs do. A preliminary experiment, performed at the suggestion of Professor Lewis, suggests that they do not. A saturated solution of chloroform (at 25°C) was found to have a viscosity within 0.2 percent of that of water. Since this solution is about $0.07M$ in $CHCl_3$, and since ΔS_2 for $CHCl_3$ is about the same as for Li^+ or F^-, we might have expected a change of about 1 percent in viscosity. That it does not occur can be interpreted only by introducing an *ad hoc* assumption, albeit a not unreasonable one. This is that the icebergs formed when a non-polar solute dissolves in water may not form firm continuous masses in which solute molecules are embedded. It would then require the presence of ionic fields or of hydrogen bonds (cf. viscosity of alcohol-water mixtures) to cause the icebergs to assume the "fused," or massive form about the solute particles which produces the increase in viscosity.

TABLE VII. Standard entropy change in e.u. per mole for the transfer of N_2O (or O_2) to pure water from alkali halide solutions of about $0.5M$ and $1.0M$ (and $2.0M$) concentration.

	Cl	Br	I	
Li	−0.24			$0.5M$ salt
	−0.40			$1.0M$ salt
	O_2			
Na	+0.34			
	+0.08			
	+0.11			
K	−0.12	−0.27	−0.36	
	−0.15	−0.33	−0.73	
Rb	−0.05			
	−0.21			
Cs	+0.04			

Values calculated by use of Eq. (23) and data quoted by Randall and Failey (see reference 42), from Geffeken (see reference 43).

Salting-Out Effect

The first is that a more extended study than has yet been made of the effect of temperature on salting-out effects may show that salting-out is to a considerable degree—perhaps even predominantly—a structural phenomenon. Some indication of this already exists, and can be simply obtained from the recalculation by Randall and Failey[42] of older salting-out data. They calculated $K = m/P$ for gases in pure water and in salt solution, where P is the partial pressure of the gas in atmospheres, and m is the number of moles of gas per 1000 grams of water in the equilibrium solution. This enables them to write $\gamma = K$ (water)$/K$ (salt solution) for the activity coefficient of the gas in the salt solution. We note, however, that since the K's are very closely constant down to infinite dilution of the gas, γ is also the true or thermodynamic equilibrium constant for the reaction

$$\text{Gas (in salt solution)} = \text{Gas (in pure water)}, \quad (21)$$

so that

$$\Delta F^\circ = -RT \ln \gamma \quad (22)$$

[42] M. Randall and C. F. Failey, Chem. Rev. **4**, 271 (1927).

gives the free energy of transfer of a mole of gas from a hypothetical solution in which there is one mole of gas per 1000 g of water in the salt solution under discussion, to the hypothetical molal solution of gas in pure water. ΔS° for this transfer, then, is given by

$$\Delta S^\circ = -\left(\frac{\partial \Delta F^\circ}{\partial T}\right)_{P, m_3} = R \ln \gamma + RT\left(\frac{\partial \ln \gamma}{\partial T}\right)_{P, m_3}. \quad (23)$$

In their Table 4, Randall and Failey give, for a number of alkali halide solutions, γ values for N_2O at 15°C and 25°C, which can be used in (23) since the molality of the salt is the same for both temperatures. The data are those of Geffcken,[43] and from the regularities which emerge from our calculations we conclude provisionally that the precision is high enough to make our results significant. These results are shown in Table VII, along with three values for O_2 in NaCl solutions. In every case, a correction has been made for the fact that, in a dilute solution of gas in salt water, the mole fraction of the gas is less than it would be in pure water in the ratio 1: $(1+(2m_3/55.51))$. This should produce a decrease in entropy when the reaction (21) takes place. The size of this term in the N_2O cases considered is either 0.036 or 0.072 e.u.

One striking result is that for N_2O, ΔS° is negative in every case except that of CsCl. The theory of Debye and McAulay[44] is easily shown to predict

$$\Delta S^\circ = -RT \ln \gamma \left[\frac{\partial \ln D_0}{\partial T} - \frac{\partial \ln \beta^*}{\partial T} + \frac{\partial \ln b_i}{\partial T} + \frac{\partial \ln V}{\partial T}\right], \quad (24)$$

β^* is defined by $D = D_0[1-\beta^* n]$ and expresses the proportionate decrease in the dielectric constant produced by one molecule of gas per cc of solution. b_i is the average salting-out radius of the ions, and V the volume of a given mass of solution. If the simplest assumptions about β^* and b_i are made, the term in $\partial \ln D_0/\partial T$ will dominate ΔS°, which will therefore be positive. This means that the results of Table VII for N_2O can be reconciled with the Debye-McAulay theory only by making rather definite *ad hoc* assumptions about the temperature dependence of β^* and of b_i. Physically, also, the customary picture of the salting-out effect is that the nonpolar gas molecules are squeezed out of the neighborhood of the ions by the preferential attraction of the latter for the polar water molecules. The existence of these regions of impaired accessibility should, other things being equal, lower the partial molal entropy of the dissolved gas by reducing the effective value of the mixing term—$R \ln N_g$. This, again, should result in a positive ΔS° for (21).

We know of no explanation for the values and trends shown in Table VII which can be made complete without some arbitrary assumptions. The negative sign of most of the ΔS° values for N_2O, however, seems to be in reasonable accord with the picture we have arrived at of iceberg formation when N_2O dissolves in pure water, and of a disturbance by ions of the structure of the solution. If the latter makes it more difficult for the N_2O to form its icebergs, then the partial molal entropy of N_2O should be less negative in salt solution than in pure water, and ΔS° for (21) should be negative, as it is. The fact that LiCl has a greater effect of this sort than KCl, and that the effect of CsCl is opposite in sign could then be accounted for by the fact that Li^+ is a competitive iceberg former, whereas Cs^+ has loosened the water so as to make iceberg formation easier for the N_2O.

The last idea would predict that ΔS° should become more positive from KCl to KI, in opposition to the observed trend. Professor Olson[45] has suggested a possible explanation of this, along the lines of his discussion[46] of certain kinetic salt effects. This takes into account the direction in which different solutes tend to orient water molecules, and would introduce here the idea that if an increase in size of positive ions, which orient water with hydrogens out, causes an increase in ΔS° for N_2O, then an increase in size

[43] W. Geffcken, Zeits. f. physik. Chemie **49**, 257 (1904).
[44] P. Debye and J. McAuley, Physik. Zeits. **26**, 23 (1925).
[45] A. R. Olson, private communication.
[46] A. R. Olson and L. K. J. Tong, J. Am. Chem. Soc. **66**, 1555 (1944).

of negative ions, which orient water with the hydrogens in, might well have the opposite effect.

Such a picture could also accommodate the fact that in NaCl, $\Delta S°$ for O_2 appears to be positive. For although N_2O and O_2 both build icebergs in pure water, there is no reason why they should be icebergs with the same orientation of the water molecules, so that the presence of NaCl might promote their formation in one case and hinder it in the other.

What has just been said, plus the question whether the peculiar dependence of $\Delta S°$ for O_2 on the concentration of NaCl is real, suggests that further experimental work in this field should prove illuminating.

Superlattice Formation

The large influence of a highly charged cation on the fluidity of its solution argues a certain mechanical strength, or rigidity, in the iceberg it forms around itself. This suggests that the other ions in the solution, if they do not themselves have too powerful a structure-breaking influence, may find some interference from this cause with their "normal" motions. For example, it may well be that in a solution of $LaCl_3$ the large iceberg which we assume to exist around the La^{+++} ion makes it more difficult for a Cl^- to come near it than would "otherwise" be the case. This would modify the Debye-Hückel ion cloud in such a direction that both positive and negative ions would be less influenced by ions of opposite sign than the Debye-Hückel theory predicts. This would account in a qualitative way for the observed positive deviation of the activity coefficient of $LaCl_3$ from the limiting law, a deviation which has always been most puzzling.[47]

This line of thought may be carried farther. If the La^{+++} and Cl^- are held apart by the icebergs around the La^{+++}, then the spacing of the ions will be more "regular" than Debye-Hückel theory predicts. If such an effect is sufficiently pronounced, we may obtain a "superlattice," and the logarithm of the activity coefficient can be expected to vary with the cube root of the concentration, as in the old Ghosh[48] theory. Figure 7 shows a representation of the very accurate data of Shedlovsky and MacInnes, in which log f is plotted against the square root and against the cube root of the concentration. The linearity of the latter plot is striking, and while it does not prove the existence of a superlattice, it does seem to make it credible. We assume, of course, that at exceedingly high dilutions the square root law holds as usual, for here the fact that the ions would only very rarely come close to each other in any case makes meaningless the prohibition of close encounters.

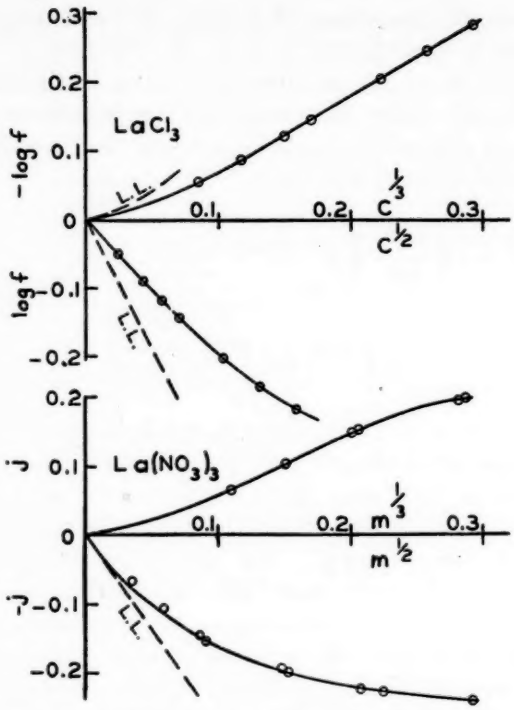

FIG. 7. Log f for $LaCl_3$ *vs.* $c^{\frac{1}{3}}$ and $c^{\frac{1}{2}}$. Data of T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **61**, 200 (1932). j for La $(NO_3)_3$ *vs.* $m^{\frac{1}{3}}$ and $m^{\frac{1}{2}}$. j values were calculated from the freezing points recorded by Hall and Harkins, J. Am. Chem. Soc. **38**, 2658 (1916).

Figure 7 also shows corresponding plots (in this case of j^7) for $La(NO_3)_3$,[49] and here it is clear that no marked peculiarity of the sort just mentioned exists. Comparison of the values of ΔS^{at} for Cl^- and NO_3^- suggests the reason. If the large structure-breaking tendency of NO_3^- bears a relation to the "strength" of the La^{+++} iceberg which enables it, so to speak, to "clear a path" for itself, then it will be able to approach the

[47] T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **61**, 200 (1939).
[48] J. C. Ghosh, J. Chem. Soc. **113**, 449 (1918).
[49] R. E. Hall and W. D. Harkins, J. Am. Chem. Soc. **38**, 2658 (1916).

La^{+++} ion more or less as envisaged in the Debye-Hückel theory.[50] Even here, however, we suspect that there is some interference with the penetration of the last one or two layers of water molecules, as otherwise there should be negative deviations from the limiting law.[51]

Here again we can obtain corroborative indications from the work of Freed.[38] He has shown that in the case of Eu^{+++} there are characteristic differences between the effects of concentration changes on the absorption spectra of aqueous solutions of $EuCl_3$ and $Eu(NO_3)_3$. These differences can be interpreted as meaning that NO_3^- ions can approach the Eu^{+++} much more freely than Cl^- ions can. Since europium and lanthanum salts must be very closely similar in the thermodynamics of their solutions, Freed's results must be taken as bearing upon the differences found between $LaCl_3$ and $La(NO_3)_3$. While, as before, many questions of detail remain to be discussed, there seems here to be some support for the superlattice picture in the chloride solutions.

There are one or two other cases, notably those of LiCl[52] and of KF,[53] in which the activity coefficient curves in dilute solutions seem to have the "wrong" shape, and in which there are present ions to which we have attributed an iceberg building tendency. Both of the salts mentioned give $\log \gamma - (c)^{\frac{1}{2}}$ curves which, if reliable, have rather extended linear portions, and it is possible that super-lattice formation occurs to some extent in their solutions. We are inclined to suspect that in all electrolytes structural effects exert a more or less pronounced influence on the ionic distribution, and that this should be listed among the factors which cooperate to produce the "normal" deviations of real electrolytes from the Debye-Hückel limiting law.[54]

[50] There is some indication that against the icebergs formed around Th^{++++}, even NO_3^- may be unable to move freely. See Prins, reference 34.

[51] H. S. Frank, J. Am. Chem. Soc. **63**, 1789 (1941).

[52] G. Scatchard and S. S. Prentiss, J. Am. Chem. Soc. **55**, 4355 (1933).

[53] G. Karagunis, A. Hawkinson, and G. Damköhler, Zeits. f. physik. Chemie **A151**, 433 (1930).

[54] There may be here also a possibility of explaining the peculiar trends found by J. Lange (Zeits. f. physik. Chemie **A168**, 147 (1934)) among the freezing points of solutions of tetraalkyl ammonium halides.

INFLUENCE OF STRUCTURE ON EQUILIBRIA IN SOLUTION

One way in which structural influences could affect equilibria is implicit in the last paragraph, since the "concentration constant" for a chemical equilibrium is altered by changes in activity coefficients, and any influence affecting the latter will be observed in the former as well. Another type of effect which structural peculiarities may be able to have on reaction tendencies in aqueous solutions is illustrated by some provisional results obtained by Professor Calvin,[55] to whom we are indebted for permission to discuss them in advance of publication.

Bjerrum[56] has investigated the equilibrium

$$Ni^{++}(aq.) + 6\,NH_3(aq.) = Ni(NH_3)_6^{++}(aq.), \quad (25)$$

and Calvin has studied this and the analogous reaction

$$Ni^{++}(aq.) + 6\,CH_3NH_2(aq.) = Ni(CH_3NH_2)_6^{++}(aq.). \quad (26)$$

He finds for (25) $\log K = 9.13$ at 23°C, and $\log K = 8.81$ at 30°C; for (26) $\log K = 8.64$ at 15°C, and $\log K = 9.12$ at 35°C. These figures correspond, for (25), to $\Delta H = -19$ kg.cal.; $\Delta S = -22$ e.u. and, for (26) to $\Delta H = +9.7$ kg.cal.; $\Delta S = +73$ e.u. This last result is so remarkable as, at first sight, to be nearly incredible, for it asserts that the methyl amine complex, though about as stable as the ammonia complex, is formed endothermically. That it is endothermal agrees, according to Calvin, with an estimate of space requirements which indicates that there is not quite enough room for the methyl groups if bond lengths and van der Waals' radii are normal. What drives the reaction forward, if the data are reliable, is the positive ΔS, which is 95 e.u. greater than that found for (25).

Allowing for some uncertainty in the numbers, it therefore appears that there are some 75–100 e.u. of entropy to account for as a difference between (25) and (26). A part of this is undoubtedly to be ascribed to the difference between the

[55] M. Calvin, private communication.

[56] J. Bjerrum, *Metal Ammine Formation in Aqueous Solutions* (Copenhagen, 1941); Chem. Abstr. **35**, C 527 (1941).

$\bar{S}_2$ values for $Ni(NH_4)_6^{++}$ and $Ni(CH_3NH_2)_6^{++}$. Comparison[25] of Mg^{++} ($\bar{S}_2 = -31.6$) and Ba^{++} ($\bar{S}_2 = +2.3$) indicates that change in size of a divalent ion is accompanied by large entropy effects, and Kraus[57] remarks that many ions which increase the viscosity of solutions give ammonia complexes which have the opposite effect. $Ni(NH_3)_6^{++}$, however, is already rather large, so that the extra size resulting from the methyl groups should fall far short of being able to account for 75 e.u. difference in $\bar{S}_2$, even after allowance is made for the likelihood that the large size of the amine complex may well cooperate with its double change to produce more structure-breaking.

As a possible explanation for the rest of the difference in $\Delta S°$ between (25) and (26) we call attention to the fact that from Fig. 3 we can estimate that ΔS of vaporization of CH_3NH_2 may be as much as 10 e.u. greater than that of NH_3. That is, the methyl group imposes an iceberg-forming tendency on the CH_3NH_2 which lowers its partial molal entropy very considerably. In the neighborhood of nickel-ammonia complex ions, however, we have assumed a structure-breaking tendency, and if this were so strong that the methyl amine, when complexed, was unable to form its iceberg, then, as compared with the ammonia complex, the methyl amine complex might form with a ΔS more positive by $6 \times 10 = 60$ e.u. This explanation is conjectural, the more so as the solutions in which the reactions are carried out are not dilute, being about $2M$ in NH_4NO_3 or $3M$ in $CH_3NH_3NO_3$, respectively. The suggestion nevertheless presents itself that further experimental work on reactions of this type might reveal the existence of structural factors which would have to be taken into account in interpreting chemical mechanisms. In particular, one is tempted to speculate on the possible influence of factors of this kind in biological equilibria, where aqueous solutions are involved of substances which carry non-polar groups.

[57] C. A. Kraus, *The Properties of Electrically Conducting Systems* (New York, 1922), p. 178.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Conduction Process in Dilute Metal-Ammonia Solutions

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October 15, 1945

THE electrical conductivity of the transparent blue dilute solutions of alkali and alkaline earth metals in liquid ammonia has long been regarded as electrolytic,[1] the carriers being the positive metal ions and "solvated" electrons, presumably NH_3^- ions,[2] the latter being responsible for the color. The great increase in the mobility of the negative carrier at high metal concentrations has been attributed to decreased solvation of the electrons.[1] While objections have been raised to this interpretation,[3] principally on the basis of magnetic susceptibility measurements, no satisfactory alternative picture has emerged.

New evidence regarding the negative carrier is offered by experimental study of highly dilute (some 10^{-4} to 10^{-3} molar) solutions of sodium and potassium when cooled to temperatures in the range from the freezing point of ammonia down to about −180°C. The solid separates as a single homogeneous crystalline phase, of a blue color which is visually identical with that of the corresponding liquid solution, and remains practically unaffected by temperature changes in the given range.

The solid solutions so prepared proved to be good electrical conductors over the entire temperature range studied. Careful measurements from −80° to −100°C indicated a marked positive temperature coefficient of specific resistance, in contrast to the negative coefficient for liquid solutions. (It is probable that this positive temperature coefficient obtains at still lower temperatures, but shrinkage and cracking of the specimens caused seriously erratic results.) There was apparently no great discontinuity in resistance at the melting point. The conductivity of a typical sample at −100°C considerably exceeded that of the corresponding liquid at −33°C. Similar observations on liquid ammonia solutions of alkali metal amides, nitrates, and iodides, which are typical electrolytes, showed that the conductivity became immeasurably small on freezing.

It seems certain that the conductivity of the solid blue solutions at such low temperatures cannot be ascribed to mass transport of ions such as Na^+ or NH_3^-, but is caused essentially by metallic conduction by virtually free electrons. (The temperature coefficient of resistance resembles that of typical metals, rather than that of semi-conductors or ionic conductors.) Accordingly, it appears likely that motion of the negative carrier in the dilute liquid solutions does not involve mass transport of solvent molecules, but merely the passage of conduction electrons. It appears logical to describe the solutions as alloys of a metal and an insulator, and to seek the explanation of the striking concentration dependence of conductivity in the well developed theory of metallic conduction.

[1] C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalog Company, New York, 1922).
[2] L. Farkas, Zeits. f. physik. Chemie **A161**, 355 (1932).
[3] A detailed discussion of the literature is given by D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944).

Product Rule Applications

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October 9, 1945

IN a recent paper on the product rule[1] Edgell implies it has been commonly considered that the product rule applied to various symmetry types separately only when isotopic substitution did not alter the symmetry, and in all other cases only to the product of the 3N-6 vibrational frequencies. He cites Herzberg's book[2] as the first place other applications have been indicated. The purpose of this note is to mention previous applications in the study of isotopic molecules of different symmetry.

Some of the best illustrations of such applications are in the study of the deuterated benzenes carried out by Langseth and Lord.[3] A wide range of symmetries was obtained by the substitution of one to six hydrogen atoms by deuterium, namely C_s, C_{2v}, D_{2h}, D_{3h}, and D_{6h}, with two kinds of C_{2v} symmetry. Their paper contains a short discussion of the product rule, including the application to the appropriate symmetry types of isotopic molecules of different total symmetry, uses it to check frequency assignments, and uses it to calculate frequencies which are forbidden to appear in the infra-red and Raman spectrum. This latter use is accomplished by applying the product rule to the concerned symmetry types in benzene (or benzene -d_6) and in a less symmetrical isotopic molecule, such as para-benzene-d_2, where the frequencies are allowed.

Another discussion of this type of application is given in a book by Hibben.[4] The discussion is general for isotopic molecules, although benzene and its deuterium derivatives are the only examples cited.

Such an application is made in the study of the deutero-ethylenes by de Hemptinne, J. Jungers, and J. M. Delfosse,[5] although without explicit mention of the product rule. The product of the frequencies of certain symmetry types in *cis*-dideutero-ethylene is compared with the appropriate product in the *trans*-form.

The product rule is discussed rather extensively, and is applied to twenty-four different polyatomic molecules and ions in a dissertation[6] on molecular structures. In

several cases, particularly methane, acetylene, benzene, and ethylene, the applications involve symmetry types of isotopic molecules of different total symmetry. Perhaps one reason that such applications are not more common is the chemical problem of preparing the isotopic molecules. Because of the equivalence of various members of a point set, many chemical reactions exchange all of them, thus retaining the symmetry of the original molecule. This is particularly true if a relatively pure deuterated product is desired.*

[1] W. F. Edgell, J. Chem. Phys. 13, 337 (1945).
[2] Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 231.
[3] Langseth and Lord, Kgl. Danske Vid. Sels. Math.-Fys. Medd. 16, No. 6 (1938).
[4] Hibben, *The Raman Effect and its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), p. 117. Some of this portion was written by E. Teller.
[5] M. de Hemptinne, Jungers, and Delfosse, J. Chem. Phys. 6, 319 (1938).
[6] Halverson, "The Use of Deuterium in the Analysis of Molecular Spectra" (Dissertation, The Johns Hopkins University, 1943). A condensed version in the form of a review paper covering all deuterated polyatomic molecules studied spectroscopically up to 1945 is to be submitted for publication in the near future.
* The earliest application of the product rule in this manner known by the author is in a paper by Redlich and Stricks, Monats. 68, 374 (1936), on some deuterated benzenes.

Structure of Soap Micelles as Indicated by X-Rays and Interpreted by the Theory of Molecular Orientation

II. The Solubilization of Hydrocarbons and Other Oils in Aqueous Soap Solutions

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October 15, 1945

IN emulsion polymerization the principal locus for the formation of polymer particle nuclei is initially in the monomer oil layers of the soap micelles[1] present in the aqueous phase. Thus, it is of interest to consider the relations and the structure of these oil layers.

The long or layer spacing (d) of the micelles as determined by x-ray measurements may be represented by either a linear (1) or a logarithmic Eq. (2), as follows:

$$d = b - ac, \tag{1}$$

$$d = k_1 + k_2 \log (1/c), \tag{2}$$

where c is the weight fraction of soap in the solution.

When a soap solution is shaken with a water-insoluble oil, the layer spacing (d) is increased by an amount (Δd) presumably caused by the inclusion of a thin layer of oil (Fig. 1) between the hydrocarbon ends of the soap molecules and a resulting expansion of the micelle in a direction perpendicular to the layers. At present the following relations are exhibited.

1. For ethyl benzene in saturated solutions at room temperature Δd is constant at 14.9A within the limits of error of the x-ray measurements over a concentration range of from 7 to 23 percent aqueous potassium laurate.

2. For undersaturated solutions Δd (and τ introduced later) is linear with respect to the amount of oil dissolved,

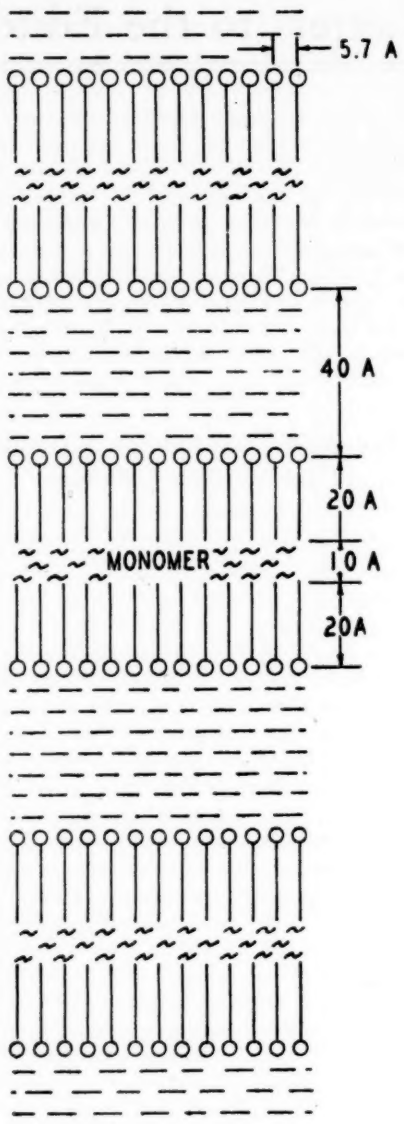

FIG. 1. Highly idealized structure of a soap micelle. Dashes represent aqueous layers.

or $\Delta d = kW$ where W is the weight of oil per 100 g of soap solution. For ethyl benzene k is 3.5 and for n-heptane 3.82.

3. The value of Δd for saturated solutions of normal hydrocarbons in 15 to 25 percent aqueous potassium laurate at 25°C decreases from 15.5A for n-hexane (6 C) to 8.0 for dodecane (12 C). Thus, the value of Δd at saturation decreases rapidly with the length of the molecule.

The chain-to-chain distance in micelles of pure soaps as calculated from the Bragg spacing varies from 4.6 to 4.7A. Since this distance is not increased, within the accuracy of the measurements, by the presence of styrene, ethyl benzene, isoprene, n-heptane, etc., little, if any, of the oil lies between the chains. In this direction the area per chain for close packing is 27 sq. A, but the mean area per chain

is greater than this, since the structure is that of a liquid in the direction of the chain-to-chain spacing. The apparent density of the solubilized oil, mostly in these thin oil layers, differs but little from the bulk density of the oil. Thus, *n*-heptane has a bulk density of 0.67981_6 g/cc at 25°C; this is equal to its apparent density in its saturated solution in 25 percent potassium laurate solution. With only a tenth as much heptane present the apparent density is only very slightly higher (0.68843_4 g/cc).

An important question now arises: is the mean thickness (τ) of the oil layer equal to the x-ray layer spacing increment (Δd)?

The apparent mean thickness, τ, is calculated by dividing the volume of oil present by the total area of the double soap layers of the micelles (Σ). This area (Σ) is the product of the area per soap molecule (30 sq. A) and $N/2$ where N is the number of soap molecules in micelles. The following relations emerge:

1. The ratio of $\tau/\Delta d$ for saturated solutions of ethyl benzene in aqueous potassium laurate increases linearly from 0.60 to 8.8 percent soap to 0.87 at 23.0 percent soap.

2. In 25 percent aqueous potassium laurate $\tau/\Delta d$ is 0.83 for ethyl benzene; 0.60 for styrene; 0.41 for *n*-heptane; and even smaller for lauryl mercaptan.

The wide divergence between τ and Δd may be attributed to several causes. Thus, it is not improbable that the activity of both the soap and the aqueous phase is changed by the addition of an oil with a consequent thickening of the micelle water layer. The molecular area of soap in the double layer is known to remain unchanged on the addition of many oils, such as hydrocarbons, etc. It is, however, affected by certain other oils such as lead tetrethyl and carbon tetrachloride, but these also give anomalous effects with respect to the layer spacing.

[1] W. D. Harkins, J. Chem. Phys. **13**, 381 (1945).

A First-Order Change which Involves the Vaporization in Two Dimensions of *N*-Heptane on the Surface of Silver*

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October 4, 1945

IN an extensive investigation of the behavior of films on *n*-heptane on the surfaces of metals a reversible first-order vaporization-condensation has been found on silver. This is of interest because changes of this order not only have never before been found on the surface of a solid, but also because many experts in the field of adsorption have doubted that such changes can occur. In most phase changes in films on solids, as well as on water, there is no heat of transformation; i.e., the changes are of the second order. Vaporization in two dimensions of oil films on the surface of water commonly involve such a heat (first order) but under certain conditions may exhibit no heat of transformation (second order). The order of such changes has been considered by Dervichian[1] and by Harkins.[2]

The first-order change occurs on silver at a pressure of 0.019 mm and a temperature of 14.90±0.05°C. However, it is not found at 25°C, so this must be above the critical temperature for the change. The relations are exhibited in Fig. 1 with volume (v) and three-dimensional vapor pressure (p) as variables, and in Fig. 2 in terms of film pressure (π) and molecular area (σ). The volume adsorbed varies from 0.00194 to 0.01380 $cm^3\ g^{-1}$, while the area per molecule varies from 310 to 2200A^2 at a film pressure of 0.18 dyne cm^{-1}.

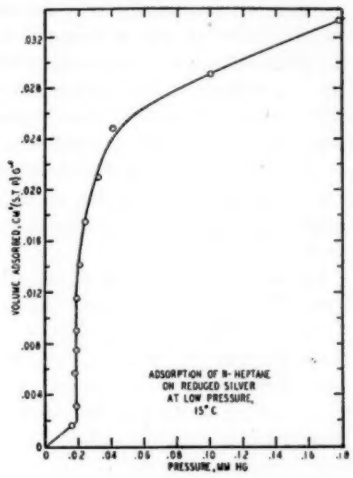

FIG. 1. The adsorption isotherm in the low pressure region of *n*-heptane on silver at 14.90°C. The first-order transition is represented by the vertical line at a pressure of 0.019 mm Hg.

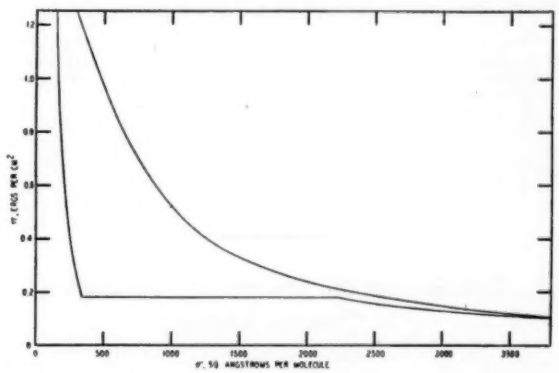

FIG. 2. The pressure-molecular area ($\pi - \sigma$) isotherms of the film of *n*-heptane on silver at 14.90° and 25.00°C. The latter is above the critical temperature of the first-order transition.

These relations are much the same as those found in the two-dimensional vaporization on the surface of water of a film of oil in which the liquid expanded phase changes into vapor. While the critical constants for the change on silver have not been determined, the following relations

must hold:

$$310\text{A}^2 < \sigma_c < 2200\text{A}^2,$$
$$288.1°\text{K} < T_c < 298.1°\text{K},$$
$$\pi_c > 0.18 \text{ dyne cm}^{-1},$$

where σ_c, T_c, and π_c are the critical area, temperature, and pressure. The values of the critical constants depend both upon the nature of the vapor and of the surface of the solid.

Except for a few discussions of adsorption based on statistical mechanics[3] practically all discussions have neglected the possibility of the occurrence of first-order changes in the films formed by adsorption on the surfaces of solids. The non-existence of experimental data which show first-order changes, in spite of the enormous amount of accumulated adsorption data, has led to a belief that such changes do not exist. That the first-order changes have not been discovered earlier is due to the fact that in the low pressure region too few experimental points have been taken to show their existence.

The silver powder used in this work was Ppt. No. 20, Hanovia Chemical Company. This was reduced in a stream of pure hydrogen and degassed at 160°C in a vacuum of 10^{-5} mm Hg for 36 hours. Its area was determined as 1.15 and 1.22 sq. meters by the use of *n*-heptane and of nitrogen, and the relative method of Harkins and Jura.[4] The former value, 1.15 m^2g^{-1}, was used in the calculation.

Several other first-order changes of this type have been discovered. These include those of water on graphite, triptane on silver, nitrogen on a fluid cracking catalyst, and *n*-heptane on ferric oxide. The last of these has been investigated in much more detail than that described here, which was, however, the first to be discovered.

* The work reported in this letter was done in connection with a more extensive investigation under contract with the National Advisory Committee on Aeronautics and under the direction of William D. Harkins and George Jura.

[1] D. G. Dervichian, J. Chem. Phys. **7**, 931 (1939).
[2] W. D. Harkins and G. E. Boyd, J. Phys. Chem. **45**, 20 (1941).
[3] For a review, see R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, England, 1939), pp. 421–444.
[4] W. D. Harkins and G. Jura, J. Am. Chem. Soc. **66**, 1366 (1944).

Efficiency of the Electrolytic Separation of Chlorine Isotopes

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October 13, 1945

IN a recent paper[1] the precise determination of the isotopic separation coefficient, α,[2] in the electrolytic separation of chlorine isotopes at a platinum anode was reported by H. L. Johnston and the writer. Suspension[3] of NaCl crystals in ethylene dibromide was employed to determine the change in isotopic composition of the chlorine. The writer's recent work on the electrolytic separation of potassium isotopes[4] afforded an opportunity to check the previously determined α value for chlorine with similar apparatus but by a different procedure.

In the present work aqueous solutions of Baker's Analyzed C. P. NaCl were electrolyzed at a platinum anode and the residual chlorine analyzed for its isotopic composition instead of the electrolyzed chlorine as in the previous work.[1] The electrolytic cell consisted of a four liter round bottom Pyrex flask to the bottom of which was sealed an extension similar to that described previously[5] which furnished a means for a flowing mercury cathode. Isotopic analyses were made in a manner previously outlined.[5] The earlier reported data[1] concerning the suspension medium, ethylene dibromide, and the suspension of NaCl crystals in this medium are applicable to the present determination. Water which was used in all reagent preparations was obtained by double distillation from an aqueous alkaline permanganate solution in a fused quartz still.

The fraction of chemical equivalents of Cl^- not electrolyzed was determined by analysis of the residue. Samples of the residual solutions of sodium chloride were titrated with standard $AgNO_3$. This furnished a satisfactory method of determining the number of residual chemical equivalents of Cl^-.

Purification of the residual NaCl for the preparation of suspension crystals was effected by boiling the residual electrolyte to dryness in a platinum container. The residue was then given two successive crystallizations from solutions prepared with double distilled water. At this point the NaCl was fused in platinum to eliminate any traces of HCl retained from the residual electrolyte. The NaCl was then given eight more crystallizations from aqueous solutions.

Standard crystals of normal isotopic composition were prepared in a manner identical with that above for the residue crystals. Purified HCl, prepared in a manner previously described,[3,6] was added in concentration equivalent to that of the residual solution from the electrolyses

TABLE I. Data for the separation of Cl isotopes in the electrolyses of aqueous NaCl.

Electrolysis number	1	2	3	4
Average electrolyte temperature (°C)	25	20	15	40
Average current density (amp./cm²)	0.060	0.080	0.040	0.060
Equivalents of Cl^- in starting material	1.5096	1.5202	1.4970	1.4803
Equivalents of Cl^- in residue	0.19437	0.22521	0.16479	0.20488
Fraction of residual equivalents of Cl^-	0.12875	0.14814	0.11008	0.13840
Current efficiency[a]	0.41	0.55	0.40	0.42
Suspension temperatures of different crystal fragments relative to standard crystals taken at zero[b]	−0.094 −0.094 −0.093 −0.090 −0.089 *I*, *I*, *I*.	−0.091 −0.091 −0.090 −0.088 −0.088 *I*.	−0.102 −0.101 −0.098 −0.098 −0.097	−0.093 −0.092 −0.091 −0.091 −0.088 *I*.
Average ΔT	0.0920	0.0896	0.0992	0.0910
Change in the atomic weight of Cl	0.00460 1.0062	0.00448 1.0065	0.00496 1.0062	0.00455 1.0064

[a] See p. 874 of reference 5.
[b] *I* indicates imperfect crystals not used to get the average ΔT.

before starting the purification of the standard NaCl. If minute traces of impurities were present, this identical purification procedure for both residual and standard NaCl would tend to eliminate errors in the ΔT's of crystal suspension.

The data for the separation of chlorine isotopes at a platinum anode in the electrolyses of aqueous solutions of NaCl are presented in Table I. The ΔT's represent all crystals prepared and suspended in the ethylene dibromide. Linear averages were taken for the computation of α.

α's for the four electrolyses were computed from the equation,

$$\alpha=\frac{\log\left[\frac{(A_{Cl}-A_{35})\{\rho_{NaCl}(A_{37}-A_{Cl})-dM_{NaCl}\Delta T\}}{(A_{37}-A_{Cl})\{\rho_{NaCl}(A_{Cl}-A_{35})+dM_{NaCl}\Delta T\}}\right]}{\log\left[F\left(1+\frac{dM_{NaCl}\Delta T}{\rho_{NaCl}(A_{Cl}-A_{35})}\right)\right]}+1, \tag{1}$$

in which F is the fraction of the residual number of chemical equivalents of Cl^-; M_{NaCl} is the molecular weight of normal NaCl; A_{Cl} is the atomic weight of normal Cl; A_{35} and A_{37} are the mass values of Cl_{35} and Cl_{37}, respectively; ρ_{NaCl} is the density of normal NaCl; d is the isothermal change in the density of NaCl when ΔT is equal to one degree; and ΔT is the suspension temperature of standard normal crystals minus the suspension temperature of crystals prepared from the residual electrolytic solution. Equation (1) is an exact solution of the equation in reference 2 in terms of the experimentally measured quantities, F and ΔT. Values used for the constants in Eq. (1) are: $A_{35}=34.980$;[7] $A_{37}=36.978$;[7] $A_{Cl}=35.457$;[8] $M_{NaCl}=58.454$;[8] and ρ_{NaCl} (at 27.63°C) $=2.16165$ g/ml;[6] $d=1.85\times10^{-3}$ g/ml/degree.

The average of these four single step electrolyses is 1.0063 which is in good agreement with the previously determined value. A linear average of the α's of the previous electrolyses and of the present ones gives 1.0061. No dependence of the α value on the cell temperature or the current density can be shown. The value $\alpha=1.0061\pm.0005$, for electrolysis at a platinum anode is constant over the temperature interval of 15° to 40°C.

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[1] H. L. Johnston and D. A. Hutchison, J. Chem. Phys. **10**, 469 (1942).
[2] α is defined by the relationship $d \ln Cl^{35}=\alpha d \ln Cl^{37}$.
[3] See footnote 2, D. A. Hutchison, Phys. Rev. **66**, 144 (1944).
[4] To appear soon.
[5] H. L. Johnston and C. A. Hutchison, J. Chem. Phys. **8**, 869 (1940).
[6] H. L. Johnston and D. A. Hutchison, Phys. Rev. **62**, 32 (1942).
[7] F. W. Aston, Proc. Roy. Soc. **A163**, 391 (1937).
[8] Eleventh report of the Committee on Atomic Weights of the International Union of Chemistry, J. Am. Chem. Soc. **63**, 845 (1941).